KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday September 28, 1907.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 28 September 1907, Dl. XVI).

CONTENTS.

H. J. HAMBURGER and E. HEKMA: "Quantitative researches on Phagocytosis. A contribution to the biology of phagocytes", p. 144.

P. VAN ROMBURGH: "The decomposition of penta-erythritol tetraformate on heating", p. 166.

J. VAN BEUSEKOM: "On the influence of wound stimuli on the formation of adventitious buds in the leaves of Gnetum Gnemon L.". (Communicated by Prof. F. A. F. C. WENT), p. 168.

A. L. W. E. VAN DER VEEN: "The system of crystallization of the diamond". (Communicated by Prof. G. A. F. MOLENGRAAFF), p. 182.

J. D. VAN DER WAALS: "Contribution to the theory of binary mixtures. VI. The plaitpoint line", p. 183.

H. KAMERLINGH ONNES and J. CLAY: "On the measurement of very low temperatures. XV. Calibration of some platinum-resistance thermometers", p. 200.

H. KAMERLINGH ONNES and C. BRAAK: "Isotherms of diatomic gases and their binary mixtures: VI. Isotherms of hydrogen between — 104° C. and — 217° C.", p. 204.

H. KAMERLINGH ONNES and J. CLAY: "On the change of the resistance of the metals at very low temperatures and the influence exerted on it by small amounts of admixtures", p. 207.

H. KAMERLINGH ONNES and G. H. FABIUS: "Repetition of DE HEEN's and TEICHNER's experiments on the critical state", p. 215.

H. KAMERLINGH ONNES and W. H. KEESOM: "Contributions to the knowledge of the ψ-surface of VAN DER WAALS. XV. The case that one component is a gas without cohesion with molecules which have extension. Limited miscibility of two gases". (Second continuation), p. 231.

J. J. VAN LAAR: "Some remarks on the last observations of Prof. H. KAMERLINGH ONNES and W. H. KEESOM", p. 238.

Errata, p 239.

Physiology. — "*Quantitative researches on phagocytosis. A contribution to the biology of phagocytes.*" By Prof. H. J. HAMBURGER and Dr. E. HEKMA.

(Communicated in the meeting of June 29, 1907.)

I. *Introduction and method of investigation.*

The investigations of which an abridged account is given in this paper [1]) are a continuation of those begun several years ago by one of us [2]), with the object of ascertaining the influence exercised by solutions of various concentration on the red corpuscles and other cells. These researches had been for the greatest part confined to the study of chemical and volumetrical alterations experienced by the cells through the modification of their media and of their significance with regard to the functions of the body. But until now, *the influence of these agents on the life of the cell itself*, had not been the object of a systematic investigation, although the plan had existed for some time and the expediency of the method had been proved [3]). The importance of such an investigation will be readily admitted. In the first place, because it enhances the value of the chemical and volumetrical researches mentioned above, and secondly, because the phenomena produced by the agency of solutions undangerous to life, are in fact nothing else but the effects of reaction, which finally will help us to penetrate farther into the chemical structure of the living cell. The red corpuscles, which were mostly used for the chemical and volumetrical researches, however, are no suitable objects for the study of the influence of reagents upon life, for they do not afford sure tests of vitality, nor is it possible to measure the value of their life functions.

We therefore looked elsewhere for our material and our choice fell on the phagocytes, for the twofold reason that they are simple, isolated cells in which it is possible to follow the effect of the chemical exchange with their natural medium, and to rate their very life by quantity; besides the phagocytosis is an essential factor in the functions of life. In support of this latter contention, we refer to the important place assigned by METCHNIKOFF to these cells in the struggle of the body against disease; a theory which he has

---

[1]) For detailed account, see "Biochemische Zeitschrift".

[2]) HAMBURGER, Zittingsverslag der Koninkl. Akad. v. Wetensch. 29 December 1883.

[3]) HAMBURGER, Het gedrag van witte bloedlichaampjes tegenover cyaankalium, Bijdrage tot de kennis der celpermeabiliteit. Feestbundel voor Rosenstein, 1902.

defended with such admirable acumen and unflagging energy. According to the same investigator, the part they play in the healthy body is no less important. The only thing therefore which remains to be done with regard to these cells, is to get a nearer insight into their conditions of life; as yet scarcely anything is known on this subject, a fact mentioned with regret by METCHNIKOFF, in the paper he read last year before the students of the University of Amsterdam, on: "Réactions phagocytaires" [1]).

The method of investigation employed by us was the following: White corpuscles from the blood of a horse, after having been transported into various media, were brought into contact with carbon and afterwards it was ascertained what percentage of the leucocytes had taken up particles of carbon. *This percentage was the measure for the degree of phagocytosis and gave the value of the influence of various agents on that function of life.*

These calculations were based on the principle that the phagacytorian power of the phagocytes present in a suspension is of unequal extent; i. e. the more detrimental the action of the agent is, the smaller must be the number of phagocytes able to take up carbon.

Our selecting a neutral indifferent substance of bacteria, had its ground in the fear that otherwise our work would have become too complicated. We here refer to the recently established fact that most kinds of bacteria, before they can be taken up by the phagocytes, must undergo a certain amount of preparation [2]). Hence it follows that not only will the intensity of phagocytosis be influenced by the agent as such, but also by the degree of preparation it has undergone. Another fact which had to be borne in mind, is that the bacteria sometimes secrete poisons which have an injurious effect on the phagocytosis.

---

[1]) "Nous ne sommes qu'an début. Lorsqu'on connaîtra mieux *la physiologie des phagocytes* (the italics are ours) on cherchera des méthodes pour augmenter l'activité de ces éléments dans la lutte contre les microbes et on cherchera d'autres pour préserver contre l'attaque des phagocytes les cellules nobles de notre corps. En poursuivant ce but, il faudra tenir compte de ce que les phagocytes sont non seulement les destructeurs des microbes, mais qu'ils sont capables aussi de s'incorporer des poisons solubles et de les rendre inoffensifs. Leur rôle n'en devient que plus important."

[2]) WRIGHT and DOUGLAS, Proceed. of the Royal Society **72**, 1903, p. 357 and later studies prepared under WRIGHT. Further HEKTOEN and RÜDIGER, Journ. of Infect. diseases **2**, 1905, p. 128 and other studies prepared under HEKTOEN.

The selection of the indifferent substance carbon, instead of the usual grains of carmine was based on the greater facility and more accurate certainty with which the taking up of carbon can be ascertained. It was also for this reason that carbon had been the substance selected in former investigations on the action of carbonic acid [1]) and the action of cyanate of potassium [2]) on phagocytosis.

On the present, as well as on the former occasion, the leucocytes used in our investigations, were taken from the blood of a horse [3]). They were obtained by shaking blood with pieces of glass in a closed bottle and straining the defibrinated blood through a piece of muslin. The red corpuscles sink to the bottom, and the serum which covers them holds all the leucocytes. When this turbid fluid has been poured off we have a suspension of leucocytes in serum; this suspension can be made richer in leucocytes, by centrifugalizing it, removing part of the clear serum and mixing the leucocytes which have fallen to the bottom, with the remaining serum. A detailed description of this method, the process of preparing the carbon, the mode of bringing it into contact with the leucocytes, and the method of determining the percentage of the cells which have taken up carbon, will be found in our article in the Biochemische Zeitschrift [4]).

II. *The effects produced on phagocytosis by the addition of water.*

Our first experiments were directed to the solution of the question in how far phagocytosis is affected by the addition of water.

With this object in view, equal quantities of the suspension of leucocytes were mixed with serum, previously diluted with known quantities of water. The following table shows the results of one of the series of experiments. It will need no further explanation.

---

1) HAMBURGER. VIRCHOW's Archiv, **156**, 1899. S. 329. Osmot. Druck u. Ionenlehre. **1**. S. 416.

2) HAMBURGER. Het gedrag van witte bloedlichaampjes tegenover Cyaankalium in ROSENSTEIN's Feestbundel. 1902.

3) At Groningen we experienced great difficulty in obtaining a regular supply of horses' blood. Mr. K. HOEFNAGEL, the Director of the abattoir at Utrecht, had the great kindness fully to meet our wants, for which we here beg to tender him our best thanks.

4) Compare also HAMBURGER, Osmot. Druck u. Ionenlehre, Bd. 1. S. 401.

TABLE I.

Effect of lessening the concentration of the serum.

Serum diluted with	Number of examined white corpuscles	Number of white corpuscles which have taken up coal	Percentage of number of white corpuscles containing coal	Decrease of the phagocytarian power
0% water	886	331	37	
20 „	754	246	32	13.5%
50 „	732	154	21	43.2 „
100 „	636	81	12½	66.2 „
140 „	530	0	0	
200 „	546	0	0	

From this table it appears that in serum, to which no water has been added, of the 886 examined leucocytes, 331 had taken up carbon, i.e. 37 %.

We must here point out that in the circulating, and also in the coagulated blood, the percentage of phagocytes is actually much smaller.

By a certain proceeding, however, we contrived that in our experiments, the leucocytes used for examination should contain a great number of phagocytes. This process is based on the fact that among the leucocytes, the phagocytes are the cells which soonest sink to the bottom. After this explanation, it will cause no surprise to find that, in normal serum, the percentage of the phagocytes which have taken up carbon, continually varies in different series of our experiments.

An addition of 20 % water, already lessens the phagocytarian power with 13½ %. In calculating this loss on an addition of 5 % water, supposing the diminution to be proportionate, the decrease of the phagocytarian capacity would have amounted to: $\frac{5}{20} \times 13.5\ \% = 3.4\ \%$. In other words, *when the osmotic concentration of the blood plasma is lessened by* 5%, *a loss which in a healthy individual may be of daily occurrence* [1]), *the phagocytarian power falls about* 3.4 %.

By the side of this great sensitiveness of the phagocytes to the increase of their percentage of water, stands the fact, as shown from

[1]) Compare a o. KOEPPE. PFLÜGER's Archiv. 62, 1896. S. 567. In his experim nts, KOEPPE noticed a decline below the mean osmotic pressure of over 10 %.

the table, that on the other hand, there are a great number of phagocytes which can stand a dilution of their serum with 100 % of water. Former experiments have proved that this dilution causes an increase in the bulk of the cells, of considerably over 30 %.[1])

We will now pass on to the following question: *Is this decrease in the phagocytosis of a permanent nature?*

In order to find an answer, we brought the white corpuscles which had been submitted to the action of diluted serum back into the normal, undiluted serum, and then tested again their power of taking up coal.

TABLE II.

After exposure to the action of diluted serum, the phagocytes are brought back into normal serum.

Serum diluted with	Number of white corpuscles examined	Number of white corpuscles which have taking up carbon	Percentage of white corpuscles containing carbon, in normal serum
0% water	500	105	21
20 „	500	99	19.8
50 „	500	107	21.4
70 „	500	96	19.2
100 „	500	78	15.6
200 „	500	61	12.2

This table shows that phagocytes, which had some time remained in serum, diluted with 20 % or 50 % water, dilutions which as the former series of experiments indicates, caused a reduction of the phagocytarian capacity of 13.5 % and 43.2 % respectively, after having been brought back into normal serum, *entirely recovered their original phagocytarian power.*

The addition to the serum of 100 % water, has on part of the phagocytes a lasting deleterious effect; the addition of 200% water is even more detrimental. Still, itis interesting to observe that, although in serum which had been diluted with 200 % water, all the phagocytes

[1]) HAMBURGER. Archiv. f. (Anat. u.) Physiol. 1898. S. 317.

had lost the power to take up carbon, after being replaced in the normal serum, over 50% of the phagocytes recovered their original capacity.

So, *the greater part of the phagocytes can support a considerable volume of water without permanent loss of their phagocytarian capacity.*

Here may be asked: On what does it depend, whether a phagocyte will regain its phagocytarian power? It is not impossible, nay, it is even probable, that here as well as in the case of the red corpuscles some lose their contents in serum diluted with 70 % of water [1]). If the quantity of water added be raised to 100 %, the number of destroyed erythrocytes will be found considerably larger. When the red corpuscles, which *have not lost their haemoglobin*, are removed from the serum diluted with 100 % of water into undiluted serum, they entirely recover; they change from small globules into biconcave discs, which even arrange themselves like piles of coins.

However, this only applies to the cells which have not lost their colouring matter. These which have actually lost haemoglobin cannot recover. Now our microscopical investigations have revealed the fact, that in serum + 70 % water, some of phagocytes lose a part of their contents: in that case we see a granular substance lying by their sides. In serum to which 100 % water has been added, the effect is more apparent still. Then the number of leucocytes which have expelled granular matter is still larger. It is easy to understand that these cells, when again placed in normal serum, have lost the power of taking up carbon. The difficulty of ascertaining this with certainty however, is very great: in the transmission there is every chance of disturbing the granular substance by the side of the cells, and it is impossible to know whether one deals with a phagocyte which has lost part of its contents or not. Anyhow, taking into consideration the striking analogy existing between white and red corpuscles, both with regard to their permeability and to the osmotic pressure of their interior substance, and even to the percentage of the volume of their watery contents [2]), we seem justified in our conjecture that the same fluid, which causes a loss of colouring matter in the least resisting of red corpuscles, also brings about the irremediate destruction of the phagocytarian power of the least resisting phagocytes.

It is a fact worthy of notice that the resisting power of the phagocytes reaches a higher maximum than that of the erythrocytes. In serum diluted with 200% water, all the erythrocytes of the horse are destroyed, and not quite half of the phagocytes.

III. *Effect on phagocytosis by the reduction of water.*

A similar method as had been used for studying the effect on phagocytosis by dilution of the serum, was now applied to ascertain the

[1]) Hamburger. Transactions of the Royal Academy of Sciences, 26th March 1885.
[2]) Osmot. Druck u. Jonenlehre I, S. 401—435.

influence of concentration. With this object in view, common salt was dissolved in the serum in quantities of 0.1, 0.2, 0.3, 0.4 % and more. The results of these experiments are shown in the following table:

TABLE III.

Effects on phagocytosis by increased concentration of the serum.

Serum in which is dissolved	The liquids in the preceding column are corresponding to:	Procentage of leucocytes which have taken up carbon	Decrease of the phagocytarian power
0 % Sod. Chl.	Sod. Chl. 0.9%	$\frac{208}{832} \times 100 = 26\,\%$	
0.1 „	„ 1	$\frac{184}{874} \times 100 = 21.5$	17.3%
0.2 „	„ 1.1	$\frac{184}{1005} \times 100 = 18.3$	29.6
0.3 „	„ 1.2	$\frac{76}{941} \times 100 = 8$	69.2
0.4 „	„ 1.3	$\frac{43}{793} \times 100 = 5.4$	79.2

Here we see that the injurious effect is very great, much greater than is the case when the osmotic concentration has been diminished. Then we observed that by diluting the serum with 20 % water, phagocytarian capacity fell 13.5 %; here we find that by raising the osmotic concentration by 10 %, the phagocytarian power is lowered by 17.3 %. This effect must already be perceptible within the physiological boundaries in which the osmotic pressure of the blood plasma usually varies in the normal body. For it may happen every day that in a normal individual the osmotic pressure of the liquor sanguinis, a few hours after dinner, is still raised by that of 0.1 % common salt [1]).

Here again, as we did before when studying the decrease of osmotic pressure, we ask whether the loss of phagocytarian power

[1]) Koeppe, l. c.

D. Schoute. Het physisch-chemisch onderzoek van menschelijk bloed in de kliniek. Diss. Groningen 1903.

See also Osmot. Druck u. Ionenlehre B. I S. 540 ff.; B. II S. 279 and 310 ff.

can be restored, by replacing the white corpuscles in the normal serum. The answer will be found in the following table.

TABLE IV.

After being exposed to the action of increased concentration, the leucocytes were replaced into normal serum.

Serum in which is dissolved	After replacement into normal serum, the phagocytarian power stands at
0% Sod. Chl.	$\frac{273}{700} \times 100 = 39\%$
0.2 „	$\frac{246}{646} \times 100 = 38.4$
0.7 „	$\frac{226}{685} \times 100 = 33$
1.2 „	$\frac{170}{567} \times 100 = 30$
1.5 „	$\frac{149}{713} \times 100 = 21$
2 „	$\frac{87}{625} \times 100 = 14$
3 „	$\frac{57}{590} \times 100 = 9$

From this table it may be seen that after exposure to the action of serum in which 0.2 % common salt had been dissolved, a solution which had lowered the phagocytarian capacity by 29.6 % (see table III), replacement in normal serum brings it back to its original value. The action of serum in which 0.7 % of salt had been dissolved, however, causes a permanent loss of phagocytosis. Still, this loss is not so great considering that, in the serum with 0.7 %, not a single cell has taken up carbon, — in other terms, the phagocytosis has been entirely paralysed.

Now the phagocytes had only been exposed for half an hour to the action of the concentrated media. This certainly may be considered long enough for the small cells to readjust themselves to their new medium. Still, it may be asked whether *after a more prolonged exposure the normal value of the phagocytarian power would be restored too.* This question is of great importance for the functions of normal life, in

which the increase of osmotic concentration often lasts longer than half an hour. For this reason, the experiments in which the leucocytes were exposed to an action of much longer duration, were made with serum containing only 0.1 and 0.2% NaCl; higher osmotic concentration does not occur in the body. The leucocytes were placed in the serum of increased osmotic concentration for 2, 24 and 48 hours, and then transferred into normal serum.

The experiment showed that after an exposure of 24 and 48 hours, the phagocytarian power had been diminished; but an *equal* decrease of vitality was also observed in phagocytes which had remained for 24 and 48 hours respectively in *normal* serum. This proved that the prolonged action of serum of increased osmotic concentration had had no *permanent* injurious effect on the phagocytarian capacity.

Thus we may conclude that, in the living body an increase in the osmotic concentration of the blood plasma, as well as a decrease of the same, has a deleterious effect on the phagocytarian power, but that the loss may be recovered; for as soon as the osmotic pressure has been restored to the normal, the phagocytes also entirely regain their inherent power.

If from these experiments we may conjecture, that what we have observed in the phagocytes, will also be applicable to other cells with semipermeable walls, it is reasonable to conclude from the results shown in tables II and III, *that the vital functions of the cell are in a large measure influenced by slight oscillations in the osmotic concentration of the environment and consequently of the cells themselves.*

IV. *Effect of simple solutions of Salt.*

1. Solutions of Sodium Chloride.

Now the question arises whether the loss of vitality described above, must be attributed to the variations of the quantity of water as such, or to the modification in the concentration of one or more of the substances.

In order to examine this question systematically, we might have alternately reduced the several elements in the diluted serum to their original concentration and then studied the extent of the improvement. But as in the mean time it had been clearly demonstrated to us that in a pure solution of Sodium Chloride of 0.9 % the phagocytes take up carbon in equal or almost equal quantities as in normal serum, we decided to abandon this mode of investigation.

Here we must incidentally remark that, after all that has been said by

LOEB [1]) and others, of the injurious action of a pure solution of a simple salt on the life of young moving larvae and the vital processes of higher animals, such as the beating of the heart and the movements of the intestines, we were at first rather astonished at the almost perfect innocuousness of similar solutions in regard to the phagocytes. However, we can easily find an explanation for this seeming inconsistency. Whenever a cell is surrounded by a simple isotonic solution of salt, two things are likely to happen: an exchange of ions may take place, thus causing a modification in the chemical structure of the cell, which interferes with certain of its vital functions. This is the case with the larvae of fundulus with the muscle of the heart and that of the intestines. A supply of specified ions is then required to restore the chemical structure of the cell to its normal state. But — and this is the second possibility — if the permeability of the cell to ions is highly limited, a pure isotonic solution of salt will not cause any, or only a very slight alteration in the chemical structure of the cell. This is the case with the white corpuscles, the slight permeability of which to ions of salts has already been demonstrated in the most convincing manner.[2])

Bearing this fact in mind, it can cause no surprise that, contrary to the results of the observations on eggs and muscles, a pure solution of Sodium Chloride leaves the phagocytarian power entirely or almost entirely intact.

Under these circumstances, for determining the influence of the water as such, it was indicated to take solutions of Sodium Chloride of various strength.

Table V shows the action of diluted solutions of Sodium Chloride on phagocytosis.

TABLE V.

Effect of hyper-isotonic solutions of Sodium Chloride on phagocytosis.

Solutions of Salt.	Percentage of leucocytes which have taken up carbon.
NaCl-sol. 0.9%	$\frac{235}{756} \times 100 = 31$ %
NaCl 0.75% = NaCl 0.9% + 20% water	$\frac{208}{741} \times 100 = 28$
„ 0.6 = „ 0.9 + 50 „	$\frac{221}{1012} \times 100 = 21.8$
„ 0.45 = „ 0.9 + 100 „	$\frac{83}{745} \times 100 = 11.1$

[1]) J. LOEB, American Journal of Physiol. **3** 1900 p. 327 and 383; **5** 1901 p. 362 Pflüger's Archiv **80** 1900 S. 229.
LINGLE, Americ. of Journal of Physiol. **4** 1900 p. 265.
Miss MOORE, Ibid. 1900 p. 386 etc.

[2]) HAMBURGER. Zeitschr. f. Biol. **35**. 1897 S. 252 and S. 280; Proceed. of the Royal Academy of Sciences 11 April 1897.
Archiv f. (Anat. u.) Physiol. 1898 S. 31 and S. 317.
VIRCHOW's Archiv **156** 1899 S. 329.
HAMBURGER and VAN DER SCHROEFF, Archiv f. (Anat. u.) Physiol. 1902. S. 251.

Here we see the marked effect of a diminution in the concentration of the salt solution.

TABLE VI.

Effect of hyper-isotonic solutions of salt.

Solutions.	Percentage of leucocytes containing carbon.	Decrease of the phagocytarian power.
NaCl 0.9%	$\frac{250}{722} \times 100 = 34.6\%$	
" 0.95	$\frac{293}{875} \times 100 = 33.5$	3%
" 1	$\frac{95}{802} \times 100 = 11.84$	60.6
" 1.1	$\frac{105}{981} \times 100 = 10.8$	69
" 1.2	$\frac{7}{990} \times 100 = 0.7$	98
" 1.3	$\frac{0}{200} \times 100 = 0$	
" 1.4	$\frac{0}{150} \times 100 = 0$	
" 1.5	$\frac{0}{150} \times 100 = 0$	

The surprisingly rapid decline of phagocytosis observed in serum of increased concentration (table III) is again clearly demonstrated in this instance.

Even the slight increase of 0.9 to 1% lowers the phagocytarian power already 60.6%. Another illustration of this rapid decline is afforded by the observation that in the 1% concentration of Sodium Chloride, the amount of carbon present in the coal containing phagocytes is far less than in those that have stayed in the solution of 0.9%.

Now, by comparing tables VI and III, we see at a glance that, when the experiments were made with a solution of Sodium Chloride of 0.9 %, to which afterwards salt had been added, *the decline in the phagocytarian power is more marked* than when they are

made in serum supplemented with an equal quantity of salt. This proves that besides the osmotic pressure, which must principally be made accountable for the decline, there is still another factor at work, *and this factor can be no other than the modification — however slight — produced by a pure solution of NaCl in the chemical structure of the phagocytes.* Some time ago, one of us, in conjunction with Dr. VAN DER SCHROEFF [1]), already demonstrated that the leucocytes the same as the red corpuscles are in any case permeable to *an*ions. It is therefore evident that, owing to their chemical structure being interfered with, the cells most lose some of their vitality (phagocytarian power) under the action of pure salt solutions, — or rather, that they should lose *more* than in an isosmotic serum.

We have submitted this hypothesis to further experiments, starting from the following reasoning: If it is a fact that in a hyper-isotonic solution of salt, the phagocytes undergo a chemical variation through exchange of ions, it must be possible to restore this loss of phagocytarian capacity resulting from their modification in their structure, by replacing them in normal serum, and that this recovery will not be complete by immersion in a 0.9 % solution of salt. The following table proves that we were correct in our surmise.

TABLE VII.

Effect of solutions of salt on the chemical structure of the phagocytes.

White corpuscles immersed for $2^1/_2$ hours in the following solutions.	Phagocytarian power after being transferred into.	
	Normal Serum	Salt solutions of 0.9%
NaCl 0.9%	$\frac{319}{942} \times 100 = 33.9\%$	$\frac{284}{811} \times 100 = 35\%$
„ 1	$\frac{258}{775} \times 100 = 33.3$	$\frac{251}{760} \times 100 = 33$
„ 1.1	$\frac{233}{790} \times 100 = 29.5$	$\frac{209}{735} \times 100 = 28.6$
„ 1.2	$\frac{202}{722} \times 100 = 28$	$\frac{175}{677} \times 100 = 26$

[1]) HAMBURGER and VAN DER SCHROEFF. l. c.

It is clearly demonstrated that the phagocytes, which have been exposed for two hours to the action of solutions of Sodium Chloride, exhibit a greater phagocytarian power when they are transferred into serum, than when they are placed into salt solution of 0.9 %.

No doubt the observation will strike the attentive reader as contradictory, that this is only the case with the phagocytes which had been exposed to the action of sodium chloride of 1 %, 1.1 % and 1.2 %, but not with those which for the same space of time had been immersed in a similar solution of 0.9 %; then the effect of this salt-solution and the serum is quite the reverse. This, however, is not actually the case; for in serum the phagocytes are likely to stick together and on this account do not offer as large a surface to the carbon as in the salt-solutions in which they remain more isolated. If then, as must be the case in an *isotonic* solution, the injurious effects of the Cl-ions of the pure salt solution are comparatively small, they may easily be exceeded by the unfavourable position of the cells caused by the serum.

When, however, by the use of *hyper-isotonic* solution of sodium chloride, the injurious action of the Cl-ions be increased, it may exceed the detractory influence of the agglomeration of the cells, and produce the results shown in the table.

With regard to these statements it may here be asked why, in *isotonic* solutions of sodium chloride, the injurious effect on the phagocytes cannot be determined, but is easily demonstrated when hyper-isotonic solutions are used, and the more readily in proportion as the concentration of the salt solutions are increased in strength. This question is very natural, because it concerns such a small increase in the considerable amount of ions of Cl or of Na already present. Here we are involuntarily reminded of the fact stated by HEDIN [1]) with regard to the red blood-corpuscles. The minute investigations of this scientist have brought to light the fact, that in isosmotic *isotonic* solutions of salt, the corpuscles possess an equal volume, but that in isosmotic anisotonic solutions their relative volume is no longer equal. HEDIN has not given an explanation of this important fact; but anyhow, it proves that simple solutions of salt, when anisotonic, exercise still another kind of action beyond that of their osmotic pressure. We propose to investigate this matter somewhat further: it is very probable that by a modification in the dissociation of the contents of the cell, an altered condition for the exchange of ions is produced.

---

[1]) HEDIN. Skandinavisches Archiv f. Physiol, 1895 S. 377.

2. Solutions of Chloric Potash.

In our description of the influence of sodium chloride, we attributed it to the ions of chlorine. This was based on the results of investigations in which we compared the action of sodium chloride and of potassium chloride, of which a few items here follow.

These investigations proved that isosmotic solutions of sodium chloride and potassium chloride have almost the same effects on phagocytosis.

TABLE VIII.

Comparison of isosmotic quantities of sodium chloride and potassium chloride.

	Percentage of leucocytes containing carbon.
Serum	$\frac{253}{722} \times 100 = 35\ \%$
NaCl-sol. 0.9%	$\frac{300}{836} \times 100 = 36$
KCl-sol. 1.15% (isot. m. NaCl-sol. 0.9%)	$\frac{258}{277} \times 100 = 34$
Serum + 0.1 % NaCl	$\frac{183}{672} \times 100 = 27$
„ + 0.127 „ KCl	$\frac{181}{715} \times 100 = 25$
„ + 0.3 „ NaCl	$\frac{45}{630} \times 100 = 7$
„ + 0.38 „ KCl	$\frac{54}{683} \times 100 = 8$
„ + 0.3 „ NaCl afterwards placed into	$\frac{184}{600} \times 100 = 30$
„ + 0.38 „ KCl normal serum	$\frac{185}{621} \times 100 = 30$

Two other parallel-experiments in solutions of 0.9 % of sodium chloride produced the following results:

$\frac{198}{863} \times 100 = 23\ \%$ of leucocytes containing carbon

and $\frac{146}{677} \times 100 = 21.5\ \%$ „ „ „ „

in the isosmotic solution of KCl 1.15 %:

$$\frac{128}{615} \times 100 = 21\ \%$$ leucocytes containing carbon

and $$\frac{165}{732} \times 100 = 22.5\ \%$$ „ „ „

Hence we may conclude, that there is no difference between the action of chloride of potassium and chloride of sodium.

3. Effect of chloride of calcium.

The great importance which, according to the most recent investigations must be ascribed to the ions of calcium,[1]) in the constitution of the fluid-matter of the tissues, induced us to test also the effect of this medium on phagocytes.

With this object in view, we dissolved various quantities of chloride of calcium in the serum of the blood of a horse and mixed the suspension of leucocytes thus obtained with carbon.

TABLE IX.

Effect of calcium chloride.

Serum +	Percentage of leucocytes containing carbon	Increase of the phagocytarian power
0% $CaCl_2$ 6 aq.	$\frac{132}{612} \times 100 = 21.2\%$	
0.01%	$\frac{225}{861} \times 100 = 26$	22.6%
0.1	$\frac{180}{652} \times 100 = 27.6$	30.2
0.5	$\frac{162}{598} \times 100 = 27$	27.3
1	$\frac{0}{724} \times 100 = 0$	

An addition of 0.01 % *of Ca Cl, 6 aq. to the serum already produces an increase of the phagocytarian capacity of* 22.6 %; by the addition of 0.1 % Ca Cl, 6 aq., the effect is somewhat

[1]) See especially the investigations of Loeb. Publications of the University of California and of Langendorff and Hueck. Pflüger's Archiv **96** 1903 S. 473; for the complete bibliography on the subject until 1904, see Osmotischer Druck und Ionenlehre B. III, S. 107 etc. Comp. also A. Netter, Importance biologique du Calcium. Paris. Masson et Cie. 1907.

greater, and by the addition of 0.5 % $CaCl_2$ 6 aq., it again decreases.

The result registered in the first instance, which is produced by the addition of 0.01 % $CaCl_2$, must be considered the most valuable, for it denotes the nearest unalloyed effect of the calcium chloride. In the experiments where quantities of 0.1 %, 0.5 % and 1 % of $CaCl_2$ were added, the increase of phagocytosis is counteracted by the unfavourable influence of the raising of osmotic pressure.

This experience is in strict accordance with the observations made by LANGENDORFF, who found that the injection of very small quantities of calcium, causes the heart to beat with greater force. We ascribe this manifestation to the action of the ion of calcium on the contractile substance, and we may conclude that the muscular fibre and the phagocytes also, are permeable to this cation.

4. Effect of citras natricus.

The frequent use which, in consequence of the experiments of WRIGHT and DOUGLAS,[1]) is made of this medium at the present day by the bacteriologists, in order to prevent the coagulation of the blood, actuated us also to experiment with this substance for the sake of determining its action on the phagocytosis. The following table gives a survey of the results.

The customary solutions of 1 % and 2 % of citras natricus in 0.9 % solution of sod. chl. were used in these experiments.

TABLE X.

Effect of citras natricus.

	Percentage of leucocytes containing carbon
(*a*) 1 cc. suspension of leucocytes + 2 cc. solution of 1% citras natr. in 0.9% Sod.Chl.	0
(*b*) 1 cc. suspension of leucocytes + 2 cc. solution of 2% citras natr. in 0.9% Sod.Chl.	0
(*c*) leucocytes from (*a*) transferred in Sod.Chl. 0.9 %	$\frac{260}{686} \times 100 = 38\,\%$
(*d*) leucocytes from (*b*) transferred in Sod.Chl. 0.9 %	$\frac{255}{731} \times 100 = 35\,\%$
(*e*) 1 cc. suspension of leucocytes + 2 cc. solution of 0.9 % Sod.Chl. (Control test)	$\frac{369}{725} \times 100 = 50\,\%$

[1]) WRIGHT and DOUGLAS, Proceed. of the Roy. Soc. **72**, 1903, p. 357; **73**, 1904, p. 128.

From the above table it is shown: 1. That in 1—2 % solutions of citras natricus in 0.9 % of Sod. Chl. the phagocytarian power is nil.;

2. that the phagocytarian capacity again *partially reappears*, when the cells are transferred into 0.9 % solutions of Sod. Chl. *The permanent decline of the phagocytarian power still amounts to* 28 %.

5. Effect of Fluornatrium.

Fluornatrium being also much used for preventing the coagulation of the blood, it seemed important to us also to study the effect of this medium on the phagocytosis.

TABLE XI.

Effect of Fluornatrium.

	Percentage of leucocytes containing carbon	
	Before being transferred into 0.9% Sod. Chl.	After being transferred into 0.9% Sod. Chl.
2cc suspension of leucocytes + 2cc NaFl 0.65% (isot. with NaCl 0.9)%	0%	$\frac{91}{677} \times 100 = 14\%$
" + 2cc NaFl 1%	0	$\frac{30}{511} \times 100 = 6$
+ 2cc NaFl 2%	0	0
+ 2cc NaCl 0.9%		$\frac{369}{725} \times 100 = 50$

Here we see that when the leucocytes have been exposed to a solution of Fluornatrium of 2 %, 1 % or 0.65 % (isot. with 0.9 % NaCl) the phagocytarian power is entirely paralysed, yea, that even after transferring of the phagocytes in a solution of 0.9 % Sod. Chl. it shows to have been entirely destroyed for ever. *Hence we may conclude that NaFl is a powerful poison for the protoplasma of the phagocytes.*

V. *Effect of acid and alkali.*

1. Effect of acid.

The important part which the alkaline reaction of the blood-plasma seems to play, not only in connexion with the degree of

oxydation taking place in the body, but also in infectious diseases, induced us to study its effects on the increase or decrease of the phagocytarian power.

The results of one of the experiment are shown in the following table.

TABLE XII.

Diminution of the alkaline reaction of the serum.

1 cc $^1/_2$ n. H_2SO_4 +	Amount of acid added	Percentage of white blood corpuscles containing carbon
9 cc serum	$^1/_{20}$ norm.	0
14 cc "	$^1/_{30}$ "	$\frac{13}{308} \times 100 = 4.3\,\%$
19 cc "	$^1/_{40}$ "	$\frac{35}{398} \times 100 = 9$
49 cc "	$^1/_{100}$ "	$\frac{165}{724} \times 100 = 21.4$
299 cc "	$^1/_{600}$ "	$\frac{255}{612} \times 100 = 41.7$
499 cc "	$^1/_{1000}$ "	$\frac{256}{530} \times 100 = 43.5$
normal serum		$\frac{227}{530} \times 100 = 43$

We observe that even the small addition of $^1/_{600}$ *n*-acid is injurious to the phagocytosis.

Now, we know that according to titration with lacmoïde, 100 c.c. horse serum in the mean is equivalent to 75.5 cc. $^1/_{25}$ *n*-acid [1]); consequently it is calculated that serum represents an alkaline fluid of $^1/_{30}$ normal.

The addition of $^1/_{600}$ *n*-acid, therefore lowers its alkaline reaction by 5 %.

Consequently, a diminution of the alkaline reaction of the serum by 5 % is already injurious to the phagocytes.

This result is in strict accordance with the injurious effect experienced

[1]) HAMBURGER, Verhandel. d. Koninkl. Akad. v. Wetensch. Second section, Vol. VI, N°. 1, 1897.

by administering acid per os, and we are fully justified in ascribing the poisonous effects of the acid, to a diminution in the process of oxydation.

The results agree also with the observations recently published by J. Loeb, on the influence of the traces of NaOH (OH-ions) on the artificial fructification of the eggs of sea-urchins. The author has clearly demonstrated that the primary cause of this effect might be found in the acceleration of chemical reactions. [1]).

TABLE XIII.

Increase of the alkaline reaction of the serum.

1cc $^1/_2$ n. NaOH +	Amount of alkali added	Percentage of white corpuscles containing carbon.
29cc Serum	$^1/_{60}$	$\frac{25}{622} \times 100 = 4$
37cc „	$^1/_{76}$	$\frac{57}{840} \times 100 = 6.8$
49cc „	$^1/_{100}$	$\frac{114}{707} \times 100 = 16$
99cc „	$^1/_{200}$	$\frac{179}{716} \times 100 = 25$
197cc „	$^1/_{400}$	$\frac{143}{531} \times 100 = 27$
399cc „	$^1/_{800}$	$\frac{149}{580} \times 100 = 25.7$
normal serum		$\frac{177}{664} \times 100 = 26.5$

It is seen from this table that, within a large margin, the addition of OH-ions to the serum does not exercise a perceptible influence on the phagocyterian power; it remains unaltered until the value is increased by $^1/_{200}$ normal: i.e., with 15 % of the original alkaline reaction. An additional supply of alkali causes a lessening of the phagocytarian power.

More pronounced still is the effect of acid and alkali on the phagocytes, when these substances, instead of being added to serum, are

[1]) J. Loeb, Pflüger's Archiev **118**, 1907, H. 3/4, S. 181.

introduced in solutions of 0.9 % *sod. chl.* A more detailed account of the results of these investigations will follow later.

We also made a number of experiments to test the influence of other media on the phagocytarian power, e.g. with *ureum*, *chinine*, *argentum colloidale*, *heterogenous serum*, etc., the results of which will appear in a subsequent paper.

Summary.

The following are the principal conclusions derived from the above described experiments.

1. The action exercised by various media on the phagocyterian power of white corpuscles, can be accurately determined by counting the percentage of cells which have taken up particles of carbon.

2. *The addition of water to the inherent medium of the phagocytes i.e. to their own serum, acts injuriously on the phagocytarian power. Even a decrease in the osmotic concentration as may daily occur in a normal individual, causes a perceptible decline in the phagocytarian power.*

So, it was shown in one of the experiments that, whilst in normal undiluted serum 37 % of the leucocytes had taken up carbon, in serum which had been diluted with 20 % of water the amount of cells containing carbon was only 32 %: this corresponds to a decline in the phagocytosis of $\frac{37-32}{37} \times 100 = \mathbf{13.5}$ %.

By the addition of 50 % water, the percentage of phagocytes containing carbon fell to 21 %; thus in this case a decrease of phagocytosis of $\frac{37-25}{37} \times 100 = \mathbf{43}$ %.

By addition of 140 and of 200 % water, the percentage of the carbon-containing leucocytes was lowered to nil, — in other words the phagocytarian power had been suspended; but only *temporarily, for*

3. *by replacing the cells damaged by the addition of water, into their own serum, the phagocytarian power is entirely or partially restored.*

So the recovery was complete, when the serum had been diluted with 20 % or 50 % of water, and only partial when 70 tot 100 % water had been added. Even when it had been diluted with 200 %,

a figure at which, it is shown under 2, the phagocytosis had been entirely suspended, — a recovery took place in the phagocytarian power to half of its original amount.

4. *The observations, here made with the phagocytes, correspond with those previously observed in the red corpuscles.*

1. The phagocytes, the same as the red corpuscles, can support a considerable quantity of water ($\pm$ 60 %) without a single cell being destroyed;

2. The modifications produced in the phagocytes by the addition of water, unless they have led to their entire destruction, may, judging from the phagocytarian capacity, be entirely obviated by replacing them in normal serum.

5. *A heightening of the osmotic concentration of the serum, as well as a lowering of the same, (comp. sub* 2) *has a very injurious effect on the phagocytosis. It was obvious that an increase of the osmotic concentration had even a more pronounced deleterious action than the decrease at the same ratio.* Already an addition of 0.1 % NaCl to the serum caused the phagocytarian power to decline 17.3 %.

By the addition of 0.4 % NaCl this decrease amounted to 79.2 % and by the addition of 0.5 % Sod. Chl., the phagocytarian power was reduced to nil; but this considerable loss was but temporary, for

6. *when the cells which had been damaged by an addition of sodium chloride to the serum, were replaced in their original blood-serum, their phagocytarian capacity was again entirely or partially restored*; entirely when only from 0.1 %—0.2 % of the substance had been added; partially when a greater amount had been used.

7. If thus, as shown under 2 and 5, the phagocytarian power is specially impaired by modification of the normal osmotic concentration of the blood-serum, this capacity will be entirely restored as soon as the blood-plasma, principally owing to the activity of the kidneys, has recovered its normal osmotic concentration. The experiments have demonstrated that this recovery is still possible after the agency of the anisotonic serum for 24 hours and more.

8. *In solutions of* 0.9 % *NaCl the phagacytarian power is almost equal to that of serum.* It considerably decreases under the action of weaker and stronger solutions of this salt, even more so than in serum which has been made isosmotic with these salt-solutions.

9. *This result leads to the conclusion that the decline of the phagocytarian capacity produced by anisotonic serum, has its cause principally in the alteration of the amount of water in the cells.*

10. *Besides the modification of the amount of water in the cells, another factor comes into play, namely the chemical change, which takes place consequently on the exchange of the contents of the cells with those of their environment and which, as a matter of course, is greater when the cell is surrounded by a simple solution of NaCl than when placed in an isosmotic serum.* This accounts for the fact, that phagocytes which have been submitted to the action of hyperisotonic solutions of NaCl, when replaced into serum, exhibit a somewhat greater phagocytarian power, than when they are transferred to a 0.9 % solution of NaCl. In the latter case they have not the opportunity, given them in the former, of regaining the ions which they have lost in the anisotonic solutions of salt.

11. *It is very probable that the ions of Ca and of OH belong to this category.*

With regard to calcium, it has been proved that by the addition to the serum of the minute quantity of **0.01 % $CaCl_2$ 6 aq**, i.e. about **0.005 % $CaCl_2$**, the phagocytarian power was raised by about **22.6 %**. The inference is that ions of calcium must have penetrated into the phagocytes.

On the other hand it may be surmised that the phagocytes will lose ions of calcium when the amount of calcium in the medium is lower than that to which the phagocytes are accustomed. This loss of ions of calcium must cause a diminution of the phagocytarian power.

We observe a similar result in the case of the OH-ions; for our experiments have demonstrated that decrease of these ions causes a lowering of the phagocytarian power. *A 5 % diminution of the alkaline reaction of the serum,* which necessarily must lower the amount of alkali in the phagocytes, *produces a noticeable decline in the phagocytarian capacity.*

12. Loeb and after him other investigators have pointed out, that a pure solution of NaCl must be considered injurious to the larvae of lower sea animals, the muscles of the heart, and those of the intestines. *This opinion does not hold for the phagocytes.* The proof of this assertion is found in the fact that in a solution of NaCl isotonic with serum, the phagocytosis is almost as powerful as in the serum itself.

This seeming contradiction may be met by the explanation that the exchange of substance between the leucocytes and the solution of NaCl, especially when the latter is isotonic with the serum, is very small; whilst in the case of other cells (citiated cells, muscular fibre cells) the conditions of the exchange of ions are not so restricted, and consequently the chemical structure of these cells is more easily modified. And it is obvious that a modification of their chemical structure causes a disturbance in their inherent functions.

13. From the facts here recorded, it is evident that in studying the action of the phagocytes on bacteria *in vitro*, the degree of osmotic concentration and of the alkaline reaction of the medium, must be taken into account. This condition has been lost sight of in several of the experiments. They ought therefore to be repeated.

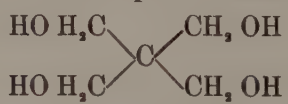
Groningen, June 1907.

Chemistry. — "*The decomposition of penta-erythritol tetraformate on heating.*" By Prof. P. VAN ROMBURGH.

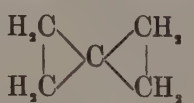
(Communicated in the meeting of June 29, 1907).

As the heating of the diformate of *s.* divinylglycol had led in such a simple manner to hexatriene 1.3.5, investigations have been set on foot in my laboratory for studying the decomposition of formic esters of polyhydric alcohols, the results of which will be gradually communicated.

If for penta-erythritol we accept the formula:

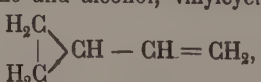


and if the reaction took place in a similar manner as with *s.* divinylglycol diformate, we might expect on heating the tetraformate[1]) the formation of a hydrocarbon of the formula:



in which occurs twice a 3-ring.[1])

[1]) GUSTAVSON C. R. **123** (1896) 242 obtained from the tetrabromide of penta-erythritol, by the action of zinc and alcohol, vinylcyclopropan:



instead of the above cited hydrocarbon.

The reaction, however, proceeds in quite a different sense, for instead of the hydrocarbon we only obtain carbon monoxide, while penta-erythritol is regenerated.

In order to prepare the tetraformate of penta-erythritol, this substance is heated with an excess (8 mols.) of concentrated formic acid in a flask connected with a condenser, in such a manner that the excess of acid distils over slowly with the water formed in the reaction. When the thermometer placed in the liquid shows 120°, the heating is stopped, and the distillation is repeated with a fresh quantity of formic acid. After this the heating is repeated twice with 100% acid. There then remains in the flask an oily liquid, which, when placed in a dish over sulphuric acid, abundantly deposits crystals after some time. These are collected at the pump, and then thoroughly pressed between filterpaper.

The solid substance thus obtained, after having been recrystallised from dry benzene, melts at 55°. After repeated recrystallisation from that solvent, the melting point rose to 57° and then remained constant.

This formate is sparingly soluble in ether; from a solution in benzene it is precipitated by ether. It has a slightly bitter taste.

On boiling with a titrated solution of potassium hydroxide the formic acid formed may be readily estimated.

Found 74.21 and 74.16% formic acid
Calculated = 74.18%.

The ultimate analysis gave the values expected for penta-erythritol tetraformate :

	Found		Calculated for $C_9 H_{12} O_8$
C	43.6	43.75	43.57%
H	5.26	5.16	4.88%

On heating this formate, a plainly visible evolution of gas commences at 220°, which is fairly strong at 230°. The gas evolved consists of pure carbon monoxide and when the evolution of gas has ceased, there remains in the flask pure penta-erythritol, which may be readily identified as such by its properties. The amount of gas evolved is that required by theory.

I wish to express my thanks to Mr. VAN ENDT, who has assisted me in these experiments with care and zeal.

Mr. RENIER, who is engaged in the study of the formates of glycols found that from 2.5 dimethyl-hexandiol 2.5, the well known tetramethyldihydrofurane, is formed by simply heating with formic acid.

On the other hand the formic ester of pentandiol 2.4 is very stable towards heat.

At about 400°, however, the ester is decomposed and a liquid is formed boiling at 42° which is most probably 1.2 dimethylcyclopropane.

Mr. VAN MAANEN, is engaged in the study of the decomposition of the formic esters of mannitol.

Utrecht, Org. Chem. Lab. University.

Botany. — "*On the influence of wound stimuli on the formation of adventitious buds in the leaves of Gnetum Gnemon L.*" By Mr. J. VAN BEUSEKOM. Communicated by Prof. F. A. F. C. WENT.

(Communicated in the meeting of June 29, 1907).

It had been observed for a long time already that adventitious sprouts were formed on the leaves of a specimen of *Gnetum Gnemon L.*, cultivated in the Botanic Garden at Utrecht.

In January 1906 my attention was drawn to this circumstance by Prof. WENT, who advised me to study the development of these adventitious sprouts, and to try to discover the origin of their formation.

The results of this investigation will be concisely communicated here.

The adventitious buds appear on the tips of the leaves, while these are still attached to the plant.

As far as I have been able to find out, the formation of these adventitious buds has never before been observed with Gnetum Gnemon, neither in its natural sites, nor in botanic gardens[1]) except at Utrecht. The Utrecht Garden possesses three specimens of Gnetum Gnemon. One of these has been continually cultivated in a hothouse where in winter the temperature is kept at about 25° C., and the air is very damp. The other two were, when I began my investigation, in an other hothouse where the temperature is lower (in winter on an average 15° C.), and the humidity less. Whereas of the former I have always obtained leaves in different stages of budformation, the other two showed the phenomenon only after they had been conveyed to the warmer and damper hothouse.

Although all three plants, apart from the formation of adventitious buds, are evidently healthy and do not make a morbid impression

1) On this point I gained information from the other botanic gardens in our country, from that at Munich and also from that at Buitenzorg.

at all, they flower very rarely. Personally I only observed it with one of the plants from the cooler hothouse. This latter plant produced one single ♂ inflorescence, which enabled me to check the accuracy of the determination.

The first external change, noticed with a leave which will form adventitious buds, is that on the tip extremely small yellow dots appear, which are seen best when light is falling through the leaf. They remind us in this respect of the oil dots in the leaves of the *Rutaceae* or *Hypericum*, but as a rule they are bigger and less densely spread than these.

With the bigger ones a hand-magnifier will show that where the dots are, the epiderm of the upper or lower side or of both together is slightly bulged, so that we have to do with small vesicles.

It will be shown presently that these vesicles are caused by the sting of a scale-insect *Aspidiotus* spec., and as such are not restricted at all to the tip of the leaf. Normally, however, it is only the tip which can form adventitious buds. The remaining part of the leafblade can only form adventitious buds when the organic relation with the tip has been disturbed in some way or other. But even then they arise apically in this part. Hence only the vesicles which have originated on the apical part of a leaf, form the introduction to the process of bud-formation.

For the sake of simplicity we shall in what follows, only mention the tip of the leaf, since the statements referring to the tip also apply to the other cases.

After some time also the region, surrounding the vesicles, becomes discoloured; as a rule the tip of the affected leaf soon becomes distinctly yellow, although in some cases it long keeps a more or less greenish tint.

At the same time with this discoloration the tip of the leaf becomes thicker. This thickening is at first not easy to observe macroscopically; gradually, however, it becomes stronger and at last generally advances so far that the tip becomes stiff and difficult to bend.

Of the yellow vesicles nothing can then be seen any longer.

The extent of this region of discoloration and thickening varies much in a basal direction; along the edge it generally extends farther basipetally than in the middle; always, however, the phenomenon is restricted to the apical part of the leaf. A new stage sets in, when the surface of the thickened leaf-tip which until now had remained smooth, on account of the swelling being even, becomes uneven: as well on the lower as on the upper surface this may as a rule be observed; on the upper surface it is generally more pronounced.

During the first weeks generally no striking changes are observed until after about a month a varying number of local elevations, yellow like the leaf-tip that produces them, becomes prominent and reveals the differentiation of special proliferating centres.

As a rule we see these grow to real knobs, especially in the direction perpendicular to the surface of the leaf.

While the knobs are still relatively small, brownish grey streaks begin to appear on their tops, which gradually extend, so that finally the whole knobbed surface becomes brown.

For some time such a knob shows nothing particular, except that it becomes larger and thicker. Next on a certain day a small opening is formed in its top, through which a small green point projects, which will grow out into a leafed sprout.

As well on the lower as on the upper surface of the leaf-tip knobs may form. Mostly they form on the upper surface, though. With some leaves I have observed knobs on both sides at the same time.

The observations on the time, needed by a leaf in order to form "ripe" knobs, after the yellow vesicles have appeared, have led to somewhat diverging resukts. The shortest period was observed with leaves on the upper branches or in the periphery of the crown, which consequently occupied the most favourable position with regard to light. On these good-sized, brown knobs had generally formed half a year after the appearance of the yellow vesicles.

Also for the question, how old and how large a knob must be in order to open and give the adventitious bud an opportunity for sprouting, no rule can be fixed. I saw one sprout five weeks after the knob had first been observed as a special elevation, while others were still closed after five to seven months.

About the size of the knobs we may state that some knobs, scarcely rising more than a millimetre above the surface of the leaf-tip, opened, while others of double and even treble the height remained obstinately closed. Yet these latter contain as well an adventitious bud and not seldom even more than one.

The microscopical investigation was for the greater part carried out on microtome preparations. For fixing the material I used the mixture: zincchloride-glacial acetic acid-alcohol, (2 grams of zinc-chloride and 2 ccm. of glacial acetic acid to 100 ccm. of alcohol of 45—50 pCt), recommended by JUEL [1]). The particular hardness of

[1]) H O. JUEL, Ueber den Pollenschlauch von Cupressus. (Flora. Bd. 93. 1904. pag. 56—62).

the leaf tissue made it necessary to treat the material, before being embedded in paraffin, during 3 to 4 × 24 hours with a 40 pCt. aqueous solution of hydrofluoric acid. After this treatment it was then washed for 8 to 10 hours in streaming water, dehydrated by the usual method and after treatment with chloroform embedded in paraffin (melting point 62° C.).

For staining the sections I used at first Haematoxylin-Delafield and saffranin, according to the prescriptions given in CHAMBERLAIN's "Methods in Plant Histology" [1]); but this method proved unsatisfactory for differentiating the very thin-walled meristem cells. Therefore I afterwards always stained with methyl green and acid fuchsin [2]), by which very good results were obtained.

A consequence of the treatment with hydrofluoric acid was that the microtome preparations were not suitable for all observations. In these cases I used hand-cut preparations, if necessary stained with Haematoxylin-Delafield.

The anatomy of the normal leaf, on which something may be found in literature with BERTRAND [3]), DE BARY [4]), SCHEIT [5]) and HABERLANDT [6]), is as follows.

The epiderm of the lower and upper surface consists of relatively small, cubical cells, the outer wall of which is strongly thickened and provided with a strong cuticle and from which capriciously shaped and canaliculate outgrowths project into the lumen of the cell. (cf. BERTRAND, l. c. Pl. II fig. 6, 7, 8.). In the epiderm of the lower side numerous, irregularly placed stomata are found.

Under the upper epiderm lies the palissade parenchyma, formed by one continuous row of cells, slightly elongated in the direction perpendicular to the leaf surface. (dimensions 13—21 μ by 21—30 μ). Between the palissade cells and the lower epiderm lies the spongy parenchyma, consisting of tubular cells, the diameter of which is on the average 18 μ, as a rule is not more than 9 μ at a partition wall between two tubes and does not reach more than 28 μ. Between the cells of the spongy parenchyma remains a system of large inter-

[1]) C. J. CHAMBERLAIN, Methods in Plant Histology 2nd ed. Chicago. 1905. pag. 30, 38 and 54.

[2]) CHAMBERLAIN. l. c. p. 40, 44 and 68.

[3]) C. E. BERTRAND, Anatomie comparée des tiges et des feuilles chez les Gnétacées et les Conifères. (Annales d. Sc. nat. Botanique 5ième série Tome XX. 1874).

[4]) A DE BARY. Vergl. Anatomie der Vegetationsorgane der Phanerogamen und Farne. (Handb. der Physiol. Botanik von W. HOFMEISTER. Leipzig. 1877.)

[5]) M. SCHEIT, Die Tracheïden-Säume der Blattbündel der Coniferen etc. (Jenaische Zeitschr. f. Naturw. Bd. XVI. Neue Folge Bd. IX. 1883.)

[6]) G. HABERLANDT, Physiologische Pflanzenanatomie 2te Aufl. Leipzig. 1886

cellular spaces. In the spongy parenchyma numerous thick-walled sclerenchyma fibres are found, which are generally ramified and often have an enormous length.

A section through a leaf-tip on which yellow vesicles are found, shows that these vesicles are caused by hypertrophy of cells of the spongy parenchyma which have there entirely lost their tubular shape and among which specimens are found, measuring 91 by 109 μ, 100 by 73 μ, 100 by 113 μ etc. Among the cells, constituting the vesicle, some are always found which in unstained preparations are conspicuous by their wall being more or less swollen and brown. In preparations, treated with acid fuchsin and methyl green, the wall of these cells is blue, those of the other cells red. Applying the usual reactions we find that these walls have become suberized. Also of the palissade parenchyma some cells may have become larger, but always in a small degree.

While in the vesicles themselves the process goes a little further still on account of partition walls forming in some of the enlarged cells, whose walls have not become suberized, also the region, surrounding the vesicles, evidently answering to a stimulus, proceeding from them, begins to undergo similar changes. Macroscopically we detect this by the more or less yellow tint, assumed by the vicinity of the vesicles. A microscopical examination of the section shows that now also outside the vesicles the cells of the spongy parenchyma are hypertrophical. As with the formation of the vesicles the chlorophyl is disorganised in the hypertrophical cells.

At this stage no function of importance may be ascribed yet to the cells belonging to the palissade parenchyma.

In most preparations now already the peculiar behaviour is noticed of those spongy parenchyma cells which border immediately on the palissade parenchyma. While the other cells of the spongy parenchyma swell as evenly as possible in all directions, those which lie immediately below the palissade parenchyma become enlarged especially in a radial direction, thus making the impression of a second layer of palissade cells. Since also in later stages they will repeatedly draw our attention, I shall in what follows call these cells subpalissade cells, instead of using the cumbrous longer definition.

This extension, especially in a radial direction, of the subpalissade cells, is illustrated by the following two tables.

A Subpaliss. cells of a normal leaf-tip	Height μ : 16	16	14.5	18	14.5	16	14	14.5	14.5	22
	Breadth μ : 31	18	16	25.5	27	27	18	25.5	31	31

B Subpaliss. cells of a yellow leaf-tip	Height μ : 33	26	38	44	47	42
	Breadth μ : 31	29	18	31	33	33

In a leaf-tip which macroscopically is distinguished, besides by the yellow colour, by a distinct thickening, the intercellular cavities of the spongy parenchyma are found to have entirely disappeared, excepting a small corner here and there. The mutual pressure which the cells consequently begin to exert on each other, causes them to assume a more polygonal shape. The cells, bordering on the subpalissade cells and often also the rows, turned towards the lower epiderm, show a tendency to stretch themselves in a direction perpendicular to the surface of the leaf. In many spongy parenchyma cells partition walls have formed.

The part, played by the subpalissade cells in the process of thickening, is generally a very important one. So I found in a leaf-tip in a place, where it was 332 μ thick (the section of a normal tip is on the average 170 μ), cell rows, formed of subpalissade cells, partitioned by two or three walls and measuring 90, 110, 115 and 127 μ in height. — The palissade rows were in these places not sensibly enlarged.

That the different tissues also in the same leaf-tip do not everywhere play the same part in the process of thickening, appears from the following figures, from measurements in two different places of the same leaf-tip;

Height of the palissade cells.	36 to 45 μ { most cells with 2 or 3 partitions	27 μ non-partitioned.
Height of the subpaliss. cells.	73 to 82 μ (mostly partitioned)	146 μ { with numerous partition walls.
Height of the spongy parench.	273 μ.	273 μ.

The special thickened outgrowths, mentioned on page 3, are caused by the same processes of proliferation which cause the thickening of the whole leaf-tip, and which in some places go on with particular activity, while the surrounding region seems to come to rest.

On the upper surface they are formed by locally strong proliferation of the subpalissade cells. Sometimes also the underlying cells, originating from the spongy parenchyma contribute to them and then it cannot be ascertained as a rule what part is derived from the subpalissade cells and what from the original spongy parenchyma. In most cases the contribution of the palissade parenchyma to the formation of the special elevations is rather unimportant.

The special thickenings on the lower surface of the leaf are entirely formed by cells which genetically belong to the spongy parenchyma but for the rest in exactly the same way as those on the upper surface. Since the cells from which they are built up, divide parallelly to the surface of the leaf and the so-formed division-

cells stretch themselves again, these special thickenings, which at first appear as small unevennesses, grow out into the knobs, already mentioned on p. 3.

How has the epiderm been able to follow the increase of surface, accompanying these thickening processes?

In a normal leaf-tip we find for the dimensions of the epiderm cells 9 to 18 μ height and 9 to 29 μ breadth, while in the epiderm, covering a special thickening, amidst cells of normal dimensions others are found which measured:

Height μ :	9	11	13	13	13	9	11	11	9	9
Breadth μ :	31	36	45.5	36	49	45,5	45.5	42	54.6	45.5

Hence some epiderm cells seem really to broaden; whether this is only an extension or active growth, I dare not decide.

Besides, the epiderm soon gives way and is rent. Like the part of the epiderm which gives way to the pressure, some cells of the tissue underneath die off, the cell-walls turning brown. In this way arise the brown streaks on the surface of the knobs which finally by extension in tangential direction of this suberizing process becomes entirely brown. A special suberizing meristem, a phellogen, is not formed.

The regular structure of these cell-hills is lost as soon as the differentiation of a meristem commences. Some cells, assembled in a small group, then enter a new stage of strong growth, which makes them conspicuous in the preparations by a more rounded form amidst the adjoining cubical cells. A number of the surrounding cells are compressed by the pressure which these primordial cells cause by their growth, and die.

Soon the primordial cells divide into a number of small filial cells with extremely thin walls and dense contents, after which the primordium has become meristem.

For answering the question in what place in a knob the meristem is formed and what is the descent of the initial cells, we have the following data. An otherwise 415 to 450 μ thick leaf-tip had by local swelling to about 840 μ, formed a knob, which by a small depression in the middle was, so to speak, divided into two halves, each of which contained a primordium of a meristem. The surface of the knob was entirely suberized to a fairly considerable depth. In one half the primordium lay 220 μ below the top of the knob and its cells in all probability descended from the subpalissade cells, in the other half the primordium lay 180 μ below the surface and was of the same origin as in the former case.

While in another case a primordium was noticed which genetically belonged to the original spongy parenchyma I found in a small knob which was still covered by an intact epiderm, and did not rise more than 85 μ above its surroundings, and in this case had been formed by special proliferation of the palissade parenchym, a distinct young meristem immediately below the epiderm. *The epiderm cells themselves however, did not take part in the formation of the meristem.*

In a word, meristem formation may take place as well by cells, descending from the spongy parenchyma and the subpalissade cells, as from such as have been formed by hyperplasia of the palissade parenchyma, the epiderm, however, plays no part. In other words: *the adventitious buds on the leaves of Gnetum Gnemon are endogenic formations.*

In the beginning the young meristem increases in size by its own active growth as well as by new cells from the immediate vicinity becoming meristematic.

When the meristem has reached certain dimensions, it partly becomes loose from the surrounding tissue. This is brought about by some of the cells, forming the transition between the meristem and the surrounding tissue, being dissolved and resorbed.

This dissolution process proceeds along the whole upper side of the meristem, so that the growing point of the adventive bud comes to be placed in a slit-shaped space.

The greater the depth at which the meristem was originally formed inside the knob, the thicker is the layer of tissue which ultimately separates the bud from the outer world and the further the development within the enclosure proceeds. This explains how it is possible that knobs, no larger than 1 millimetre, open, while much larger ones remain persistently closed.

The appearance of two meristems within the same knob is a very common occurrence; once I found as many as four meristems in one knob.

The buds assume a green colour while they are still entirely enclosed within the knob and hence must have the power, like the germinating plants of Ephedra and the Coniferae, to form chlorophyl independent of light.

The sprouts growing out of the adventitious buds always remain short and tender. The biggest I observed reached a height of about 3,5 centimetres and consisted of a stem with 5 internodes (including the basal part) of which the upper one reached the greatest length (almost 2 centimetres), while the leaflets on the last node became

largest (about 3 cms. long). The position of the leaves is alternating, the innervation of the leaf the typical one for Gnetum Gnemon[1]). The leaflets on the first node as a rule remain scale-shaped; in some cases, however, they develop to leaflets, differentiated into stalk and blade.

Although in the axils of the leaflets axillary buds are certainly formed, I never saw the adventitious sprouts ramify themselves, except in a single case, when, as I surmise, of the basal piece of an adventitious sprout the terminal bud did not develop for some reason or other, and instead the buds in the axils of the scale-leaves sprouted.

On a differentiation of histogens at the vegetative cone I have not been able to form a definite opinion from my preparations of adventitious sprouts.

The numerous attempts which I made, in order to induce the adventious sprouts to produce roots, have all failed. This agrees with the circumstance that in my preparations I have never been able to discover anything that resembled root-formation. The sprout-carrying leaves which had been planted in wet sand did not form roots either. As far as I know formation of adventitious roots does not occur at all with *Gnetum Gnemon*.

A connection between the vascular system of an adventitious sprout and the nerve system of the mother leaf is established by procambial bundles, formed by cells of the tissue, situated between the meristem and a leaf bundle.

As a rule we find as the first indication of this vascular bundle connection in the immediate vicinity of very young meristems even, some tracheids and cells, changing into them. The degree of development, reached at a certain moment by this vascular bundle connection, is not directly dependent on the degree of development of the adventitious bud in question, but seems to me to stand in close relation to the distance between meristem and leaf bundle and to the diameter of this latter. When a complete connection has been established we see the vascular bundles of the adventitious sprout within the knob in which the bud has formed, bend towards each other and unite with a more or less cylindrical group of locally formed vessels and tracheids, the ramifications of which are connected with the vascular bundles of the mother leaf.

When describing the changes, macroscopically observed with a

[1]) Viz. Nr. 3 of the leaf nervations, distinguished by KARSTEN for the species of Gnetum [G. KARSTEN, Untersuchungen über die Gattung Gnetum. I. (Ann. du Jardin Bot. de Buitenzorg Volume XI. 1893. p. 195—218)].

leaf in which adventitious buds are forming, it has already been briefly stated that the yellow vesicles, initiating the process of bud-formation, are caused by a scale-insect, *Aspidiotus* spec.

That suspicion fell on this *Aspidiotus* had a very simple reason. Although not nearly all the leaves, showing yellow vesicles, carried scale-insects, yet the reverse was generally true and it soon became apparent that the leaves, carrying scale-insects generally also had some yellow vesicles.

But unexpected difficulties were experienced when it was attempted by means of microtome preparations to obtain certainty and a clearer insight in what had been rendered probable by macroscopical observation. A great difficulty was that the majority of the insects refused to stick to the bits of leaf from which the microtome preparations were going to be made. While a great part already loosed their hold during the treatment preceding the embedding itself, their example was followed by most others when they were put into the melted paraffin. It was supposed that perhaps the reason of this was that the scale-insects, when coming into the fixing solution, withdrew their suction organ from the tissue of the leaf, possibly on account of a pre-mortal reactional movement. After this unfavourable result the leaves carrying the insects were always treated before fixation with an anaesthetic, namely aether. This precaution, however, did not materially improve the results.

Among the microtome preparations which I obtained in spite of these difficulties, there is not a single one in which a scale-insect may be seen in a sucking position. But always in the places were an insect was on the leaf, in the tissue the changes were found which we described as characteristic for the yellow vesicles.

Here also hypertrophy, accompanied by disorganisation of the cholorophyl, of cells, belonging to the mesophyl; some of these cells have brown walls. Also in the epiderm on which the scale-insect is found, some cells are found, the walls of which are suberized and which besides are sometimes slightly swollen.

I was more fortunate with hand-made preparations, some of which show the suction apparatus of the scale-insect inside the leaf tissue. From these we see that in the yellow vesicles those cells, the wall of which has become suberized, have been in direct contact with the suction apparatus of the scale-insect and that the other cells, which become hypertrophical, only react to a stimulus, exercised by the wounded cells. On the character of this stimulant action we shall speak presently.

That here the enlargement of the cell should take place at the

expense of its own contents, as is stated for many similar hypertrophical processes, is not the impression I received. Although in many of the very strongly hypertrophical cells a large central vacuole may be observed, yet I saw nowhere reduction of the protoplasm to a very thin wall-lining. The nucleus does not show any deviation and the cell-wall does not become perceptibly thinner.

That the sting of the scale-insect not only causes the formation of the yellow vesicles but through them also all further changes, including the formation of the adventitious buds, has become clear to me by:

1. the microscopical examination of a very large number of preparations, relating to these stages;

2. the continued observation of a number of leaves on the tree, showing that those leaves on which scale-insects or the yellow vesicles caused by them, were seen, underwent the above described changes, while the control leaves remained free from them. On Sept. 13, 1906, the top of that plant which forms adventitious buds most strongly and one of its branches were each surrounded by a muslin balloon, after they had first been carefully inspected and cleaned. These balloons were supported by skeletons of galvanised iron wire and closed below by pulling them on to a pad of cotton wool, placed round the sprout. At the top of the plant were then only young leaves, on the branch full-grown ones, all of them free from scale-insects and vesicles. The balloon, surrounding the top of the plant had repeatedly to be replaced by a bigger one as the top grew.

On January 22, 1907, the balloon was removed from the branch and the leaves were examined. Of two of these leaves the extreme part of the top had turned yellow. A microscopical examination of these leaf-tips showed, however, that here was no initial stage of bud-formation. Hypertrophical cells, such as we ought to have found in this case in the mesophyl, were not present. The yellow colour was caused by the dying of the tissue, the cell-contents then discolouring.

On May 10 the top of the plant was liberated. A number of full-grown leaves which at the beginning of the experiment were still young and young leaves at lateral sprouts which during the isolation had been formed by sprouting of the axillary buds, were now seen. All these leaves were perfectly normal, healthy and strong with a normal green colour; on none of them anything could be detected of yellow vesicles or spots, of none the top showed any discoloration or thickening. The isolation by means of the muslin balloon

had not hindered these leaves at all in their normal development. Only scale-insects and other animals had been prevented from settling on the leaves with the formerly described result.

Similar tumours as the yellow, thickened leaf-tips of *Gnetum Gnemon* really are, have also been repeatedly observed with other plants and described under the name of "yellow specks" (Gelbfleckigkeit), oedemata or intumescences. The word "Intumescentia" was introduced into phytopathological nomenclature by SORAUER with the definition [1]: "Intumescentia" sind "diejenigen Erscheinungen, die das gemeinsame Merkmal haben, als kleine knötchenförmige oder drüsige Auftreibungen der Blätter aufzutreten, die meist an diesen Stellen gelb verfärbt erscheinen und eine aussergewöhnliche Zellstreckung ohne wesentliche Zellvermehrung zeigen". That the thickened leaf-tips of *Gnetum Gnemon* are not indeed "kleine Auftreibungen" and do present "wesentliche Zellvermehrung" need not necessarily prevent us from counting them among the intumescences, since as well very large [2]) or mutually coalescent [3]) as typically hyperplastic [4]) intumescences have been described for other plants.

We cannot now deal with the very divergent views of different investigators about the cause of the formation of intumescences; we will only mention that in most cases it has been stated that a high temperature and great humidity of the air are essential factors.

Experiments enabled me to form an idea about the character of the stimulus exerted by the scale-insects on the tissue of the leaf of *Gnetum Gnemon*, on which the formation of the intumescences is the reaction. After I had tried artificially to produce intumescences in leaves by mechanically wounding them in all sorts of ways and treating them with poisons, without obtaining the desired result, I arrived at the conclusion that either my method of wounding, compared with that of the scale-insects, was too coarse or that the insect injected some stimulating substance into the leaf. In order to settle these points the following experiments were carried out: 1). In

---

[1]) P. SORAUER, Die symptomatische Bedeutung der Intumescenzen (Bot. Zeitg. 48 Jahrg. 1890. p. 241).

[2]) H. v. SCHRENK, Intumescences formed as a result of chemical stimulation. (Missouri botan. garden. 16th ann. report. 1905. p. 125).

[3]) Miss G. E. DOUGLAS. The formation of intumescences in potatoplants. (Bot. Gazette Vol XLIII. 1907. p. 233.)

[4]) E. KÜSTER, Uber experimentell erzeugte Intumescenzen. (Ber. deutsch. bot. Ges. Bd. XXI. 1903. pag. 452). P. SORAUER, Ueber Gelbfleckigkeit. (Forsch. a. d. Geb. d. Agrik. Phys. h. v. Dr. E. WOLLNY. Bd. IX. 1886. pag. 387). and Intumescenz bei Solanum floribundum. (Zeitschr. f. Pflanzenkrankh. Bd. VII. 1897. p. 122).

the leaf-tips extremely small wounds were made by means of the sterilised, very fine point of an injection syringe. 2). The same was done after the point had first been stuck into yellow vesicles, caused by the scale-insects. 3). A number of yellow and thickened leaf-tips were ground in a mortar and a very small portion of the so obtained pulp, mixed with some diluted glycerin, injected in several places in leaf-tips. 4). The same operation as in 3 was applied after the pulp had first been heated to 100° C.

The result was exactly the same in *all* cases.

After some ten days small, brown specks were visible in the wounded places, which afterwards could still increase somewhat in size. A month after the wounding the brown specks had become surrounded by a very thin, more or less transparent, yellow margin. The brown specks were formed by the cells which had died in consequence of the wounding, and the walls of which had turned brown. In the yellow margin a complex was found of relatively small cells, leaving no intercellular cavities. These cells had thick walls and their protoplast still contained remnants of the chlorophyl grains. The complex was formed by hyperplasia of the whole mesophyl. On the border between this complex and the normal tissue some cells of the spongy parenchyma had become greatly enlarged, their chloroplasts having become disorganised. After another month it was noticed that the leaf-tips in the neighbourhood of the wounded spots assumed a somewhat yellow colour, which gradually became more and more distinct. Microscopically it could be stated that where externally this yellow discoloration was visible, the tissue round the wounded spots had undergone precisely the same changes as take place round the yellow vesicles, caused by the scale-insects, namely a general hypertrophy of the cells of the spongy parenchyma, while here and there even a partition wall had already been formed in the enlarged cells.

As was stated above, this result was obtained in all cases, also in those in which small wounds had been made without anything else. From which we may conclude that the leaf of *Gnetum Gnemon* may be stimulated to the formation of intumescences and hence of adventitious buds by wounding, provided this is very light and that consequently the process must be regarded as a reaction on a *wound stimulus*.

In a disease of carnations which also consists in the formation of a sort of intumescences [1]) and for which it has been shown by

---

[1]) H. v. Schrenk l. c. p. 39.

Woods [1]) that it is caused by the sting of aphides, among others, Woods thinks the growth of the yellow, thickened spots must be ascribed to the diffusion of an irritant, injected by the insect [2]).

That a similar hypothesis is superfluous for the "stigmonose" of *Gnetum Gnemon*, appears clearly enough from our experiments. The specific point about the wound, made by the suction organ of the scale-insect is only that it is so trifling. Only a few cells, namely those which are distinguished in the yellow vesicles by brown walls, have undergone the direct consequences of it, while the whole subsequent formation of the intumescences takes place as a reaction on the stimulating action, proceeding from these few wounded cells.

Kuster [3]) calls all cataplasms after vulneration, as far as they have a parenchymatical character, callus. According to this terminology also the tissue of which the thickened leaf-tips of Gnetum Gnemon consist, is a "callus" and the buds, formed in them, are callus-buds [4]).

Why the two plants from the cooler hothouse did not form callus or buds on their leaves, is now also clear. The Aspidiotus, playing such an important part in this formation of callus, is also found in the cooler hothouse; but for callus-formation the chief condition is humidity. This condition was only to some extent fulfilled by the cooler, but completely by the hotter house, while also the higher temperature in this latter could not but favour the formation of callus with these tropical plants.

Why only the apical part of a leaf is capable of forming callus and buds, may be explained in the following manner. The small wound causes an afflux of nutrient matter in an apical direction. If now an accumulation of this matter, which is necessary for the hyperplastic formation of callus, shall be possible, the afflux must not be able to pass by, i.e. it must be stopped apically of the wound. And this condition is normally only fulfilled in the tip of the leaf, in another part of the blade only when the organic relation with the tip has been disturbed.

Botanical laboratory at Utrecht.

---

1) A. F. Woods, Stigmonose: a disease of carnations and other pinks. (Bull. no. 19. U. S. Dept. Agr. Div. Veg. Phys. and Path. 1900).

2) l. c. p. 24.

3) E. Küster, Pathologische Pflanzenanatomie. Jena. 1903. p. 154.

4) See also: E. Küster, Histologische und experimentelle Untersuchungen über Intumescenzen. (Flora oder allgem. bot. Zeitg. 96 Bd. 1906, p. 527—537).

Crystallography. — *"The system of crystallization of the diamond"* by Mr. A. L. W. E. VAN DER VEEN, candidate mining engineer. (Comm. by Mr. MOLENGRAAFF).

(Communicated in the meeting of June 29, 1907).

There still exists some doubt about the system of crystallization of the diamond. Although the tetrahedral hemihedrism of the diamond is pretty generally accepted, still the opinion that it belongs to the regular system, also finds support.

The existing uncertainty is caused by the lack of physical research with regard to this question. Such a research into the existence or non-existence of polarity of the trigonal axes has now been made. With that object in view the trigonal axes of the diamond were tested for pyro-electricity according to P. P. KOCH's method [1]). Tourmaline, boracite and quartz, which evinced strongly pronounced pyro-electrical characteristics, were used as testminerals. The result arrived at is absolutely negative. The diamond is not pyro-electric, and the trigonal axes do not possess polarity.

Besides, researches were made into the crystalline form of the diamond out of a collection of 367 uncut diamonds collected by Mr. MOLENGRAAFF. Practically all types of crystallization were represented here, to explain which tetrahedral hemidedrism for the diamond had been accepted in numerous writings of GROTH, SADEBECK, MARTIN and others. The result of this investigation, which is not yet at an end, is that a rational explanation of all irregular and apparently tetrahedral-hemihedral crystalline forms of the diamond can be found in the peculiar octahedral lamellar structure of the diamond.

On this ground it may be accepted that the diamond crystallizes in the holohedral division of the regular system.

---

[1]) P. P. KOCH, Ueber eine neue Methode zur Untersuchung auf Pyroëlektricität. Inaug. Dissert. München, Mainz 1902.

Physics. — "*Contribution to the theory of binary mixtures.* VI. *The plaitpoint line.*" By Prof. J. D. VAN DER WAALS.

Continued. See p. 123.

By the plaitpoint line we understand the continuous series of points, in which the mixture is in the plaitpoint state. If we think the points of the surface of saturation determined by the coordinates T, p and x, then the plaitpoint line is a curve lying on this surface, and its projections on the planes of coordinates are expressed by: $p = f_1(T)$, $p = f_2(x)$ and $x = f_3(T)$. If the surface of saturation is given by the coordinates T, v and x, its projections have the form: $v = f_4(T)$, $v = f_5(x)$ and $x = f_6(T)$. The two surfaces of saturation mentioned may be derived from each other by the aid of the relation $p = \varphi(x, v, T)$. If we have the first mentioned surface, the substitution of p leads to the second. However, we might also have eliminated T, and obtained a surface of saturation of the form $F(p, v, x) = 0$, also one of the form $F_1(p, v, T) = 0$. A point of saturation being determined and known in all respects if the 4 quantities T, x, v, and p are known and the equation of state giving a relation between these 4 quantities, we may imagine as many surfaces of saturation as the number of combinations of 4 quantities three and three. The number of projections of the plaitpoint line is then the number of combinations two and two. For the direction of the projections $\frac{dT}{dx}$, $\frac{dp}{dx}$, $\frac{dv}{dx}$, $\frac{dp}{dT}$, $\frac{dp}{dv}$, and $\frac{dv}{dT}$ present themselves for consideration, which of course, are not independent of each other.

The best known shape of the plaitpoint line is that for which the initial point lies in the critical point of the first component, and the final point in the critical point of the second component.

In this case there is a point in which the plaitpoint line begins, and another in which it terminates; but such initial and final points lie necessarily in such places as are to be considered as natural boundary points. Thus initial and final points might also occur for boundary volumes ($v = b$) — but a plaitpoint line can never have an initial or final point for arbitrarily chosen value of v and x. Thus in the case that there is minimum or maximum T_k the mentioned well-known shape of the plaitpoint line will, it is true, make its appearance only in a certain point with gradual increase or decrease of the temperature for certain definite value of T — but such a point is then necessarily a double plaitpoint, and the plaitpoint line itself retains its character of continuous series of points; the double

plaitpoint mentioned is then an homogeneous double plaitpoint. If then in the v, x-projection the plaitpoint line is drawn, it proceeds again continuously from the left to the right side — and this continues to be the case also when the plaitpoint line mentioned has more intricate properties, e. g. when there are two heterogeneous double plaitpoints, as discussed in "Contribution etc." and also treated in These Proc. March 25, 1905, p. 621 and These Proc. June 24, 1905, p. 184. However, besides this plaitpoint line, another is possible. The latter does not cross from the left side to the opposite side. So only the possibility is left either that it is a closed curve in the v, x-projection, or that it begins and terminates on the borders $v = b$.

We shall proceed to discuss some properties of the special points of this line, particularly of the double points of this line. KORTEWEG has demonstrated that these double points are of two kinds. Either it is a double point in which two homogeneous plaitpoints originate or coincide — or it is a double point in which this is the case for two heterogeneous plaitpoints. Though physically such plaitpoints bear such different characters — mathematically they satisfy the same criteria, and on the plaitpoint line such an heterogeneous double point is the transition point for a series of plaitpoints which might be realized, and for a series of unrealisable plaitpoints.

Minimum or maximum temperature for the plaitpoint line.

If we suppose a double plaitpoint to originate or to disappear on the ψ-surface at a certain value of T, two plaitpoints are found at somewhat higher or lower value of T. This holds both for the case that the double point is an homogeneous and an heterogeneous double point, as we shall briefly call them. For the plaitpoint line $\frac{dT}{dx}$ and $\frac{dT}{dv} = 0$ in this case. But for an homogenous double point $\frac{dT}{dp}$ is also $= 0$. This property follows from the shape of $\frac{dp}{dT}$, which has been derived in Verslag Kon. Ak. v. Wet. Deel IV p. 20 and p. 82 because $\frac{d^2v}{dx^2_p} = 0$ in an homogeneous double point (Contribution etc. These Proc. March 30, 1907, p. 745). For an heterogeneous double point $\frac{dT}{dp}$ is not equal to 0, as also appears from the value given for $\frac{dp}{dT}$, as for such a double point $\frac{d^2v}{dx^2_p} = 0$, but $\frac{d^2v}{dx^2_p} = \frac{d^2v}{dx^2_q}$. That in an heterogeneous

double point $\frac{dT}{dp}$ is not equal to 0, is also immediately seen when we consider that for such a point also $dp = 0$, and $\frac{dT}{dp}$ appears therefore in an indefinite form, the value of which we shall presently determine. Hence $\frac{dv}{dx} = \left(\frac{dv}{dx}\right)_p$ for such a double point, which is not the case for an homogeneous double point.

Of the 6 differential quotients which come in for discussion, three are equal to 0 for an homogeneous double point, and three are left the value of which is still to be determined, viz. $\frac{dv}{dx}$, $\frac{dv}{dp}$ and $\frac{dp}{dx}$.

If we write:

$$\frac{dv}{dx} = \frac{\frac{dT}{dx}}{\frac{dT}{dv}}$$

$$\frac{dv}{dp} = \frac{\frac{dT}{dp}}{\frac{dT}{dv}}$$

and

$$\frac{dp}{dx} = \frac{\frac{dT}{dx}}{\frac{dT}{dp}},$$

in all these three expressions both numerator and denominator is equal to 0. If in the first we differentiate numerator and denominator with respect to x, in the second with respect to v, and in the third with respect to p, we find:

$$\frac{dv}{dx} = \frac{\frac{d^2T}{dx^2}}{\frac{d^2T}{dv^2}\frac{dv}{dx}}$$

$$\frac{dv}{dp} = \frac{\frac{d^2T}{dp^2}\frac{dp}{dv}}{\frac{d^2T}{dv^2}}$$

and

$$\frac{dp}{dx} = \frac{\frac{d^2T}{dx^2}\frac{dx}{dp}}{\frac{d^2T}{dp^2}}$$

or

$$\left(\frac{dv}{dx}\right)^2 = \frac{\frac{d^2T}{dx^2}}{\frac{d^2T}{dv^2}}, \quad \left(\frac{dv}{dp}\right)^2 = \frac{\frac{d^2T}{dp^2}}{\frac{d^2T}{dv^2}} \text{ and } \left(\frac{dp}{dx}\right)^2 = \frac{\frac{d^2T}{dx^2}}{\frac{d^2T}{dp^2}}.$$

We may verify these properties by writing for the immediate neighbourhood of the minimum or maximum plaitpoint temperature:

$$T = T_1 \pm \alpha (x - x_1)^2 = T_1 \pm \beta (v - v_1)^2 = T_1 \pm \gamma (p - p_1)^2,$$

in which the sign + holds for minimum value of T, and reversely the sign — for maximum value.

From this follows:

$$\alpha (x-x_1)^2 = \beta (v-v_1)^2 = \gamma (p-p_1)^2,$$

or

$$\pm (x-x_1) \sqrt{\alpha} = \pm (v-v_1) \sqrt{\beta} = \pm (p-p_1) \sqrt{\gamma},$$

and

$$\frac{dv}{dx} = \pm \sqrt{\frac{\alpha}{\beta}}, \quad \frac{dp}{dv} = \pm \sqrt{\frac{\beta}{\gamma}} \text{ and } \frac{dx}{dp} = \pm \sqrt{\frac{\gamma}{\alpha}}.$$

As $\frac{dv}{dx} \times \frac{dp}{dv} \times \frac{dx}{dp} = +1$, we have to take all the signs positive, or one positive and two negative. Thus in the case that there is minimum or maximum plaitpoint temperature, and we choose the direction of x such that $\frac{db}{dx}$ is positive, $\frac{dv}{dx} > 0$ and $\frac{dp}{dx} < 0$, and so also $\frac{dp}{dv}$ negative. It is, however, not always the case that $\frac{dp}{dv}$ is negative. Thus for a plaitpoint line with maximum value of p, $\left(\frac{dp}{dT} = 0\right)$ also $\frac{dp}{dx} = 0$ and $\frac{dp}{dv} = 0$. So in such a case reversal of the sign of $\frac{dp}{dv}$ must take place.

If we examine the criteria for an heterogeneous double point, we have in the first place $\frac{dT}{dx} = 0$ and $\frac{dT}{dv} = 0$. Then $\frac{dT}{dp}$ is not equal to 0. But in its stead there are two other differential quotients which

are equal to 0. From $\frac{dp}{dT} = \frac{dp}{dx}\frac{dx}{dT}$ follows, if we take into consideration that $\frac{dp}{dT}$ has a finite value, and $\frac{dx}{dT} = \infty$, that $\frac{dp}{dx}$ must be $= 0$, and also $\frac{dp}{dv} = 0$. That p has maximum or minimum value in the case of an heterogeneous double point has already been represented by us in a drawing. (These Proc. March 25, 1905, p. 621, and June 24, 1905, p. 184). So of the 6 differential quotients for the projections of the plaitpointline 4 are zero. Two are left whose value is to be determined, viz. $\frac{dp}{dT}$ and $\frac{dv}{dx}$.

If we write: $\frac{dp}{dT} = \frac{\frac{dp}{dx}}{\frac{dT}{dx}}$, we find by differentiation of numerator and denominator:

$$\frac{dp}{dT} = \frac{\frac{d^2p}{dx^2}}{\frac{d^2T}{dx^2}}.$$

If we write: $\frac{dv}{dx} = \frac{\frac{dT}{dx}}{\frac{dT}{dv}}$, we find:

$$\left(\frac{dv}{dx}\right)^2 = \frac{\frac{d^2T}{dx^2}}{\frac{d^2T}{dv^2}}.$$

What follows may serve as a verification. Let us again write as holding in the immediate neighbourhood of the double point:

$$T = T_0 \pm \alpha (x-x_0)^2 = T_0 \pm \beta (v-v_0)^2$$

and

$$p = p_0 \pm \gamma (x-x_0)^2 = p_0 \pm \delta (v-v_0)^2.$$

For minimum value of T and p the positive sign must be chosen, and reversely. So we have the following relations:

$$\alpha (x-x_0)^2 = \beta (v-v_0)^2,$$

and

$$\gamma\,(x-x_0)^2 = \delta\,(v-v_0)^2$$

from which

$$\frac{\alpha}{\gamma} = \frac{\beta}{\delta}.$$

Further

$$\frac{T-T_0}{\alpha} = \pm\frac{p-p_0}{\gamma}.$$

In this last equation the sign $+$ must be chosen, if, as is the case, T and p have at the same time either maximum or minimum value. We find then:

$$\frac{dp}{dT} = \frac{\gamma}{\alpha}$$

and

$$\frac{dv}{dx} = \pm\sqrt{\frac{\alpha}{\beta}} = \pm\sqrt{\frac{\gamma}{\delta}}.$$

That this value of $\frac{dv}{dx} = \left(\frac{dv}{dx}\right)_{p,T}$ follows from the derivation.

So we find a definite value for $\frac{dp}{dT}$, and as no lower value of T exists for minimum value of T, and no higher value for maximum value, the p,T-projection of the plaitpoint curve must possess "cusps". That this value of $\frac{dp}{dT}$ is positive, and so p and T are at the same time maximum or minimum, follows inter alia from the equation:

$$dp = \left(\frac{dp}{dv}\right)_{xT} dv + \left(\frac{dp}{dx}\right)_{vT} dx + \left(\frac{dp}{dT}\right)_{vx} dT.$$

For, as $\frac{dv}{dx} = \frac{dv}{dx_{pT}} = -\frac{\left(\frac{dp}{dx}\right)_{vT}}{\left(\frac{dp}{dv}\right)_{xT}}$, this equation reduces to:

$$\frac{dp}{dT} = \left(\frac{dp}{dT}\right)_{vx}$$

Other special points of the plaitpoint curve.

It appears from the form for $\frac{dp}{dT}$ (Versl. Kon. Ak. Deel IV p. 20) that also the case that $\frac{dp}{dT} = 0$ is possible, and for some mixtures a maximum value of p in the p,T-projection has been experimentally

shown. As $\frac{dp}{dT} = \frac{dp}{dx}\frac{dx}{dT} = \frac{dp}{dv}\frac{dv}{dT}$, we derive that in this case also $\frac{dp}{dx} = 0$ and $\frac{dp}{dv} = 0$, save in exceptional cases. Then p is the highest, or the lowest pressure that can occur on the plaitpoint curve. Of the 6 differential quotients 3 are again equal to zero, and 3 others are again to be determined, viz: $\frac{dx}{dT}$, $\frac{dv}{dT}$ and $\frac{dv}{dx}$. We find then from:

$$\frac{dx}{dT} = \frac{\frac{dp}{dT}}{\frac{dp}{dx}}$$

$$\left(\frac{dx}{dT}\right)^2 = \frac{\frac{d^2p}{dT^2}}{\frac{d^2p}{dx^2}}$$

From

$$\frac{dv}{dT} = \frac{\frac{dp}{dT}}{\frac{dp}{dv}}$$

we find:

$$\left(\frac{dv}{dT}\right)^2 = \frac{\frac{d^2p}{dT^2}}{\frac{d^2p}{dv^2}}$$

And from:

$$\frac{dv}{dx} = \frac{\frac{dp}{dx}}{\frac{dp}{dv}}$$

we find:

$$\left(\frac{dv}{dx}\right)^2 = \frac{\frac{d^2p}{dx^2}}{\frac{d^2p}{dv^2}}$$

which may be again verified from the equations:

$$p = p_1 \pm \alpha(T - T_1)^2 = p_1 \pm \beta(x - x_1)^2 = p_1 \pm \gamma(v - v_1)^2$$

For plaitpoint lines which do not run from $x = 0$ to $x = 1$, and which therefore either form a closed figure, or run from a point of

the line $v = b$ to another point of this line, the value of x may be maximum or minimum. Then $\frac{dx}{dT}$, $\frac{dx}{dv}$ and $\frac{dx}{dp} = 0$, and the three remaining differential quotients must be determined — and lastly also v might be maximum or minimum; then $\frac{dv}{dT}$, $\frac{dv}{dp}$ and $\frac{dv}{dx}$ would be equal to zero, and $\frac{dT}{dx}$, $\frac{dp}{dx}$ and $\frac{dp}{dT}$ would have to be determined.

Three phase pressure and final point of the three phase pressure on the plaitpoint line.

If at a certain temperature three phase pressure exists, there must be a hidden plaitpoint on the ψ-surface, as appears from the foregoing remarks. If the spinodal curve is closed on the side of the small volumes there is moreover a realisable plaitpoint, and there can even be another realisable plaitpoint if the temperature is above the T_k of one of the components. Let us call x_1 and v_1, x_2 and v_2, x_3 and v_3 the compositions and volumes of the three phases, assuming the first two to be liquid phases and the third to be a gas-phase, and let us put $x_2 > x_1$. Now three cases may occur, viz.: $x_3 > x_2 > x_1$; $x_2 > x_1 > x_3$ and $x_2 > x_3 > x_1$. The first case occurs when the gas phase contains more of the second component than each of the liquid phases, and so when $\left(\frac{dp}{dx}\right)_{vT}$ is always positive; the second case when the gas phase contains less of the second component, and so when $\left(\frac{dp}{dx}\right)_{vT}$ is negative, and the third case requires that the line $\left(\frac{dp}{dx}\right)_{vT} = 0$ runs between the two liquid phases. Of the first case an example may be found in the mixture water in SO_2, mixtures of ethane and some alcohols (above methylalcohol) constitute an example of the second case, and of the third case the mixture water and phenol is an example.

As we have an equilibrium which is independent of the size of the volume, when for a mixture of 2 substances there exists equilibrium of 3 phases, the formula of CLAPEYRON may serve for the computation of the value of $\frac{dp}{dT}$, and we may put:

$$T\frac{dp}{dT} = \frac{W}{u}$$

if W represents the heat which is released with decrease of volume when part of the middle phase is converted into the state of the

two other phases, and u the degree of this decrease of volume. We arrive at the same result if we follow the course (Verslag Kon. Akad. v. Wetensch. Deel V, p. 482) indicated there, viz.:

$$\frac{dp}{dT} = \frac{\begin{vmatrix} 1 & x_1 & \eta_1 \\ 1 & x_2 & \eta_2 \\ 1 & x_3 & \eta_3 \end{vmatrix}}{\begin{vmatrix} 1 & x_1 & v_1 \\ 1 & x_2 & v_2 \\ 1 & x_3 & v_3 \end{vmatrix}} = \frac{(x_1-x_3)(\eta_2-\eta_3) - (x_2-x_3)(\eta_1-\eta_3)}{(x_1-x_3)(v_2-v_3) - (x_2-x_3)(v_1-v_3)}.$$

We find the same equation when we have three phase equilibrium for a binary system of solid, liquid, and gaseous. And the course of the line $p = f(T)$ is then known. It is a line, consisting of two branches lying above each other, which smoothly pass into each other at a certain maximum temperature, and the upper branch of which possesses maximum pressure. In this case, however, the course is simpler. For the equilibrium of solid, liquid, and gaseous two branches occur; on one branch the liquid is richer in one of the components than the solid body, and on the other branch the reverse. Where these branches meet, the value of x has the same amount for the solid body and for the liquid, and in that point the line $p = f(T)$ has an element in common with the melting-point line. This is seen from the value of $\frac{dp}{dT}$, if e. g. $x_2 = x_3$ is put in it, in which case $\frac{dp}{dT} = \frac{\eta_2-\eta_3}{v_2-v_3}$. And it has, therefore, often been stated as a fixed rule, that when two phases have the same concentration, the variation of equilibrium with the temperature depends only on these two phases, and is independent of the third. Also for equilibrium of 2 liquid phases and one gas phase, however, equality of concentration may occur between two phases. Thus one of the liquid phases may get the same concentration as the gas phase, or the two liquid phases may get the same value of x. Then the above mentioned rule does not hold. When a solid body has the same concentration as a liquid, and e.g. $x_2 = x_3$, then η_2 is not equal to η_3, and v_2 not equal to v_3. Then there are, indeed, two phases of the same concentration, but not two *identical* phases. But when a liquid phase has the same concentration as a gas phase this expression means that in the three phase triangle one of the sides has been reduced to zero, and these two phases have become identical. Then we find

after division of numerator and denominator by $x_2 - x_3$:

$$\frac{dp}{dT} = \frac{\eta_1 - \eta_3 - (x_1 - x_3)\left(\frac{d\eta_3}{dx_3}\right)_{pT}}{v_1 - v_3 - (x_1 - x_3)\left(\frac{dv_3}{dx_3}\right)_{pT}}$$

or

$$T\frac{dp}{dT} = \frac{W_{13}}{v_{13}}.$$

It appears from the form for $\frac{dp}{dT}$, that this value is equal to $\left(\frac{dp}{dT}\right)_{x_3}$, if a section is made through the surface of saturation for $x = x_3$.

In other words: The three phase triangle in its extreme position touches the section mentioned — and to this we might also at once have concluded. It will also be immediately seen, that the coinciding of the points x_2 and x_3 of the three phase triangle takes place in a plaitpoint, and that therefore the final point of the line $p = f(T)$ lies on the plaitpoint line. Then we have a plaitpoint in the point where x_2 and x_3 coincide, and the p, T-projection of the plaitpoint line being the envelope of the p, T-projection of the sections of the surface of saturation for constant values of x, the plaitpoint line and the p, T-projection of the sections touch, and so also the final point of the p, T-projection of the three phase pressure, as in that final point the last element of this pressure coincides with the section mentioned. This contact has not yet been taken into consideration in former diagrams. If there are two final points of the three phase pressure, then there are two separate portions of the realisable portion of the plaitpoint line, which are joined by the three phase pressure, the meeting-points being again *cusps*, just as is the case with the hidden portion of the plaitpoint line. Now, however, rises the following question. We know from the shape of the section of the surface of saturation at given value of x, that in the simplest case it consists of two branches, and that on the upper branch the value of $\frac{dp}{dT}$ may also be negative. Can now also $\frac{dp}{dT}$ be negative for the three phase pressure? As far as I know this has never been observed; but the observations on the rise of the three phase pressure with the temperature, and the other circumstances, viz. the values of x and v, have been only little examined

as yet. If it should be possible that $\frac{dp}{dT}$ becomes negative, and for the present I do not see any reason to consider this impossible, this can only take place in the case of a plaitpoint line descending with the temperature. Accordingly the final point of the three phase pressure, so the plaitpoint, lies on that part of the section of the surface of saturation which lies between minimum pressure and critical point of contact, and it is known, that then also the plaitpoint line must descend in its p, T-projection, because it is the envelope of the sections of the surface of saturation. If $\frac{dp}{dT}$ is negative at the final point, this value must have passed through 0; this will then require that no heat is released with conversion of the middle phase into the two others, and so that if heat is released with conversion into one of the two extreme phases, the conversion into the other extreme phase is attended by heat-absorption [1]). And without further investigation this cannot be pronounced as impossible.

Finally we point out that $\frac{dp}{dT}$ cannot become infinite. For this it would be required that the denominator is equal to zero without this being the case with the numerator. Then the area of the three phase triangle must be equal to zero or the 3 points must lie on a straight line. This is the case when two points coincide, but then the numerator is also equal to zero. Now a p-line — for the three points always lie on the same isobar — can indeed be intersected by a straight line in 3 points, but in this case this would have to occur in the same three points with a q-line; this observation will most likely suffice to put down this case as one that does not occur.

So we have in the p, T-projection of the threephase pressure a curve which, at least as a rule, ascends with the temperature; under every point of this line is a point of the plaitpoint line (hidden point) and above every point is a second point of this line (realisable point). This second point is wanting if the plait should not be closed at the bounding volume.

Shapes of plaitpoint lines (p, T-*projection*).

According to the above considerations I shall describe a possible shape of plaitpoint line for the case of two components, for which

---

[1]) The diagrams p. 126 Cont. II, in which the value of v_{21} and w_{21} for coexisting phases has been represented, must be supplemented, when also incomplete miscibility is assumed.

the ratio $\frac{T_{k_2}}{T_{k_1}}$ is a high value, and for which the temperature, at which $\frac{d^2\psi}{dx^2} = 0$ has contracted to a point, is much higher than T_{k_1}. As an example take the mixture helium and hydrogen investigated by KAMERLINGH ONNES and KEESOM partly experimentally and further theoretically, or the mixture helium and water. As, however, there are two shapes possible, I shall describe them both, not stating as yet, which of these shapes is the correct one in these cases.

As b for hydrogen will be higher than b for helium, helium is the first component. In the first place we observe that there must be a complex plait for $T < T_{k_1}$, which extends over the whole width. $\frac{d^2\psi}{dv^2} = 0$ has closed on the helium side for $T > T_{k_1}$; but $\frac{d^2\psi}{dx^2} = 0$ is a closed curve, which extends outside $\frac{d^2\psi}{dv^2} = 0$ on the helium side, and so there is intersection of $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$. The spinodal curve, which remains near $\frac{d^2\psi}{dv^2} = 0$ on the side of H_2, moves further away from this line as we approach the helium side, and remains also outside $\frac{d^2\psi}{dx^2} = 0$. I shall continue to assume that the spinodal line remains closed on the side of the small volumes. The changes which must be made if this should not be the case, will be easily applied in the result at which we arrive. Then there are three plaitpoints for this $T > T_{k_1}$. With very small difference of T and T_{k_1} there is first the ordinary plaitpoint on the helium side; and further there are two heterogeneous plaitpoints, viz. a realisable one at the very small volumes, and a hidden one (see inter alia figs. 12 and 13 of the preceding communications).

If now the first mentioned plaitpoint should coincide with the hidden one, as is assumed in the discussion of these figures, only one single plaitpoint would remain; but another, more intricate case is possible. If $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$ are quite detached, as will happen with increasing temperature, the spinodal line may viz. either continue to run round the two curves, as I have repeatedly drawn, or it may split up between the two curves. For splitting it will be required that they are so far apart that a point is found between them, in

which not only $\frac{d^2\psi}{dx^2}$ and $\frac{d^2\psi}{dv^2}$ are positive, but the product is equal to $\left(\frac{d^2\psi}{dxdv}\right)^2$ — which may the sooner take place when the line $\left(\frac{dp}{dx}\right)_{vT} = 0$ is in the neighbourhood. In this case there originate two new realisable plaitpoints. Then there are 5 plaitpoints at somewhat higher temperature, because 2 new ones have been added to the three above mentioned ones. And now, as I demonstrated when I discussed such a splitting up, at somewhat higher temperature the hidden plaitpoint will coincide with one of the newly formed realisable ones, and vanish as a couple of heterogeneous plaitpoints. So there are 3 realisable plaitpoints left viz. one that is the plaitpoint of the half of the plait (transverse plait) on the hydrogen side. And the two others, which are the upper and lower plaitpoint of the half of the plait which has got detached (longitudinal plait). In other words: one half is a plait that surrounds the curve $\frac{d^2\psi}{dv^2} = 0$, and the other half runs round $\frac{d^2\psi}{dx^2} = 0$. In this half $\frac{d^2\psi}{dx^2} = 0$ performs in many respects the function which $\frac{d^2\psi}{dv^2} = 0$ performs as a rule. The splitting up of the spinodal line, so that a closed longitudinal plait detached itself, can, therefore, take place in such a way that this longitudinal plait is found at temperatures at which $\frac{d^2\psi}{dv^2} = 0$ still exists for the same value of x, but is then restricted to very small volumes (mixtures of water and phenol); or it may take place in such a way that $\frac{d^2\psi}{dv^2} = 0$ no longer exists for the same value of x, but then the volumes need not be so very small. We might say: the detaching might take place in such a way that the two parts of the plait exist above or by the side of each other.

Moreover the case may occur that $\frac{d^2\psi}{dv^2}$ has quite disappeared, and $\frac{d^2\psi}{dx^2}$ alone exists. Then only a longitudinal plait is found. This can only take place for temperatures above T_{k_1} and T_{k_2}, and if what I have called T_g, is larger than T_{k_1} and T_{k_2}.

In fig. 27 I have drawn the p,T-projection of the plaitpoint line, which in the v,x-plane is again a line which proceeds continuously from the left to the right side. At T_k for H_1 there are three points

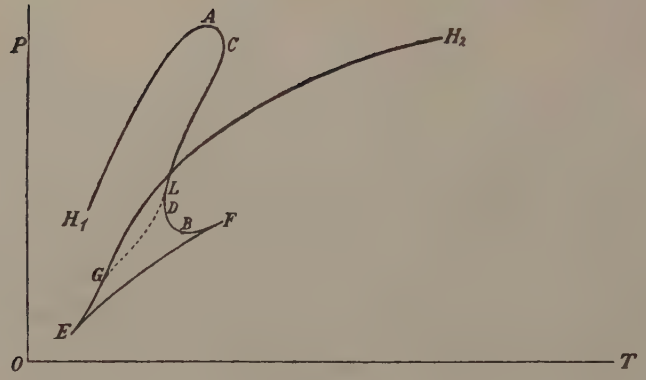


Fig. 27.

of this line; the downmost is the hidden plaitpoint lying between E and F. The place of the points E and F has been arbitrarily chosen, so that it may also be possible that E must lie more to the right than T_{k_1}. At the value of T_D, the splitting temperature, 2 new points appear. At T_F a couple of heterogeneous plaitpoints unite. At T_C the detached longitudinal plait would disappear. Between T_C and T_D there are two plaitpoints for the detached plait. The three phase pressure runs between G and L, the extremity L having been chosen such that the point D (splitting point) lies below the three phase triangle, and can, therefore, not be observed. Hence only the following 3 parts can be realized by means of the experiment: 1. H_2G, 2. H_1. ACL, 3. GL. And now, if the hypothesis that the plait is closed on the side of the limiting volumes, should be incorrect, we have only to open the upper part at A and C, and to make the open branches run asymptotically towards infinitely high. So this plaitpoint line is essentially the same as that with the double point which I have drawn. Only one of the branches, i.e. the left branch, has in addition got a maximum and a minimum pressure, and a maximum and a minimum temperature. If we drew the T,x-projection, there would be 2 maxima and two minima — also in the p,x-projection. But the v,x-projection remains simple. If the plait is closed at the limiting volumes, there is a minimum volume, in

[1]) In this figure the shape of the plaitpoint line has been drawn when really the spinodal line could run between $\frac{d^2\psi}{dv^2}=0$ and $\frac{d^2\psi}{dx^2}=0$. Further investigation will have to decide whether or no this complication can occur. If it occurs, the righthand side of the plait (transverse plait) will be much narrower, then when this complication is not met with. In the latter case the righthand part of the plait is a complex plait.

the opposite case two points for which $v = b$, come in its stead. For neither with an homogeneous double point, nor for an heterogeneous double point, $\left(\frac{dv}{dx}\right)_{pl} = 0$. And in the point in which $\left(\frac{dv}{dx}\right)_{pl} = 0$ or $\left(\frac{dx}{dv}\right) = 0$, (see p. 185) $\frac{dp}{dT}$ has not a value which presents any particularity.

The second form will differ from the one described here in so far that the temperature at which the detaching of the longitudinal plait takes place, is assumed to be equal to T_{k_2} (critical temperature of the second component).

This may take place if the temperature at which $\frac{d^2\psi}{dx^2} = 0$ disappears, is not only higher than T_{k_1}, but also higher than T_{k_2} (a case to which I alluded already before in these Contributions).

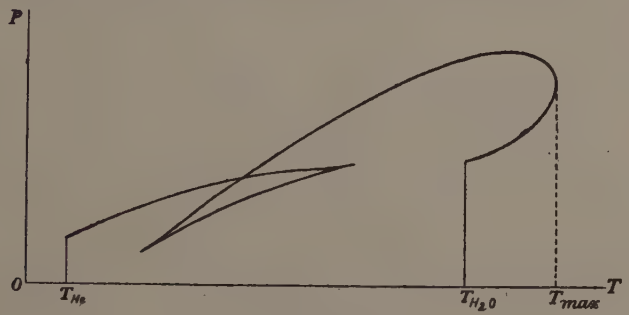


Fig. 28.

Then the p,T-projection is given by fig. 28. The highest temperature which then occurs, is that at which $\frac{d^2\psi}{dx^2} = 0$ disappears.

That for the mixture helium and hydrogen the second shape of the plaitpoint line can occur, and that therefore T_g can be $> T_{k_2}$, follows immediately from the formula for the value of T_g (These Proc. May 24, 1907) viz.:

$$MRT_g = 2\,\frac{a_1 + a_2 - 2a_{12}}{b}\,x(1-x)\,\frac{1-y}{(1+y)^2}.$$

For the case, namely, that a_1 and a_{12} may be neglected, and $b_1 < b_2$ and $x > \frac{1}{3}$, we find really $T_g > T_{k_2}$. Thus we find for $x = 0{,}4$, which belongs to $\frac{b_1}{b_2 - b_1} = 0{,}3704$, $MRT_g > \frac{8}{27}\frac{a_2}{b_2}$. For still higher value of x, this value of T_g would be found still higher, but

if $a_1 + a_2 - 2a_{12}$ becomes appreciably smaller than a_2, this may, of course, be different. In this case the plait remains a complex plait as far as $T = T_{k_2}$. At this value of T has $\frac{d^2\psi}{dv^2} = 0$ disappeared, and $\frac{d^3\psi}{dx^3} = 0$ still exists. So above T_{k_2} the complex plait is to be considered as a longitudinal plait.

If in the case described above we have a plaitpoint line that proceeds continuously in the v,x-plane, starting on the lefthand side in the critical point of the first component, and terminating in the critical point of the second component, though a maximum value of x, and then also a minimum value may be possible, still another case is possible, and most likely this case is met with in the mixture water and phenol. Of course the first mentioned line, which starts and terminates in the critical point of the components, must continue to exist, if we continue to assume that the plait remains closed on the side of the limiting volumes. Else it splits up into 2 parts, which I, however, consider as two parts of one and the same branch of the plaitpoint curve. If another branch is possible, it must be a separate closed curve — which, however, if the plait is supposed open on the side of the limiting volumes, may be considered as starting in a point of the line $v = b$, and terminating in another point of this line. We meet with this case when the longitudinal plait detaches itself at a temperature which is lower than T_{k_1} and T_{k_2}. As has been described above, the longitudinal plait will have quite retreated to volumes smaller than those of the liquid branch of the binodal line of the transverse plait at a certain value of T higher than the temperature of detaching. Then the three phase pressure no longer exists, and the first mentioned branch of the plaitpoint line, which joins the critical points of the components, has its simplest shape. In fig. 29

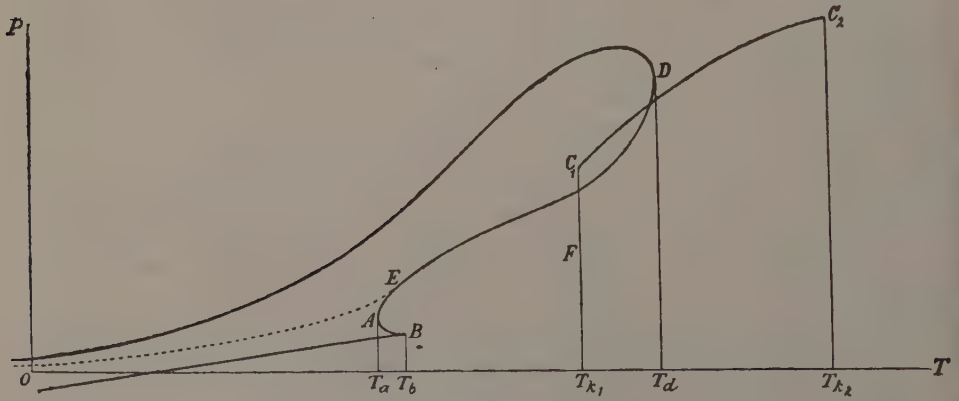


Fig. 29.

the p,T-projection has been drawn. At $T = T_A$, which is lower than T_{k_1} and T_{k_2}, the detaching takes place, and there is an homogeneous double point. At $T = T_b$ there is an heterogeneous double point, and at T_d again an homogeneous double point. If we suppose the longitudinal plait to be open towards $v = b$, p_D must be thought infinitely large, and the upper part of this second branch disappears. Without doubt the three phase pressure line, which terminates in E, will have its other extremity, i. e. its initial point, at $T = 0$.

We should have a very simple and remarkable case of a closed curve for the second branch of the plaitpoint line if the lowest temperature at which an heterogeneous double point is formed, lies little below the temperature at which this double point vanished again — and this temperature lies below T_{k_1} and T_{k_2}. Then also the temperature at which again an heterogeneous double point exists,

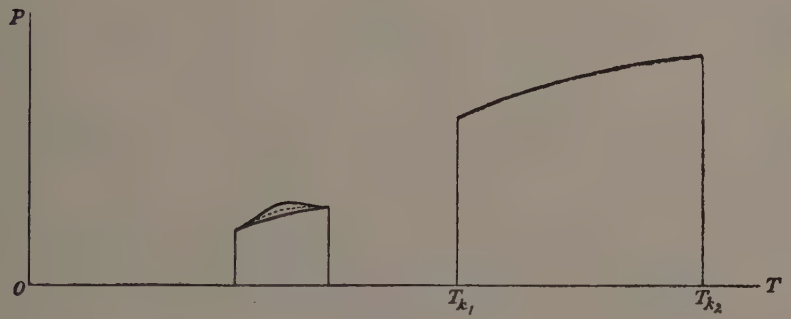


Fig. 30.

will lie only little higher than the first. Fig. 30 gives then again the p,T-projection for such a case. There can then be a phree phase pressure indicated by a dotted line. Then the liquid begins to split up into two phases at a temperature lying much below T_{x_1} and T_{x_2}, becoming homogeneous again at somewhat higher temperature — at least if the value of x has been chosen between that belonging to the extremities of the three phase pressure. In the v,x-projection we have then a small closed figure with maximum and minimum volume.

So many different shapes of plaitpoint lines, however, may be deemed possible, that they would require a special study. If they are found by the experiment, I expect that the rules given in these contributions, will prove sufficient to render them intelligible.

However, I intend shortly to indicate the circumstances in which the forms discussed are met with, more fully by means of some mathematical developments.

Physics. — "*On the measurement of very low temperatures. XV. Calibration of some platinum-resistance thermometers.*" By Prof. H. KAMERLINGH ONNES and J. CLAY. Communication N°. 99^b from the Physical Laboratory at Leiden.

(Communicated in the meeting of June 29, 1907).

§ 1. *Introduction.* The investigation on the variation of the resistance of metals (pure ones and those with known admixtures) set on foot many years ago (see Comm. N°. 77 § 1 These Proc. Febr. 1902) at Leiden, comprises besides the determination of the galvanic resistance of conductors made of the different metals, also the determination of the expansion for each of these metals. We have only little advanced as yet with the latter part of this investigation, the expansion has only been investigated for platinum, which was chosen as standard metal, and then only down to — 182°. [1]) We hope shortly to publish a Communication on the expansion down to — 252° C. For the present, however, the knowledge of this expansion is not yet of much importance for the investigation of the variation of the specific resistance with the temperature. When in this investigation we descend to very low temperatures, the correction for the expansion becomes so small compared with the disturbance in consequence of other influences which are still further to be investigated, that we may disregard it for the moment. [2])

The investigation consists then in the calibration of different resistance thermometers. The wires treated in this Communication being chiefly of importance to us as resistance thermometers, we have inserted their calibration in this series.

---

[1]) In Comm. N°. 85 (These Proc. April 1905) it was observed for the first time that in order to represent the expansion of glass from — 180° to 0° a formula of the second degree with other constants was required than for the range from 0° to + 100°. We found this confirmed in Comm. N°. 95^b (These Proc. Sept. '06), and also applicable to platinum, for which a formula of the third degree, as we gave one for glass, proved necessary between — 180 and + 100°. Afterwards (Dec. '07) SCHEEL, who was at first (Zeitschr. f. Instr.k. April '06) of opinion that a formula of the second degree could be found for platinum between — 190° and + 100°, come to the same opinion as we, and gave the three constants for platinum. Our formula of the second degree for platinum between 0° and —180° quoted by SCHEEL was used by us to prove, that for platinum between —180° and +100° a formula of the second degree is *not sufficient*, but that a formula of the third degree is required. In order to show this with given values at + 100°, 0° and — 190° observations at a temperature about halfway between 0° and — 190°, as our — 87°, are more suitable than observations at a temperature between 0° and + 100°, as those by SCHEEL at + 56°.

[2]) Here it is left entirely undecided whether the variation of the resistance with the temperature is not in close connection with the expansion.

§ 2. *Particulars on the comparison and on the investigated wires.* In these calibrations we have taken the platinum wire which was compared with the hydrogen thermometer in Comm. N° 95c (These Proc. Sept. '06) and which we shall call Pt_I, as standard. We determined the variation of the resistance of the other wires by bringing them together with Pt_I at the desired temperature, and by then comparing their resistance with that of Pt_I. The two platinum wires Pt_{III} and Pt_V were brought in the same cryostat (see § 4 Comm. 95c) together with Pt_I, and whereas the temperature was kept constant with one resistance according to the indication of the WHEATSTONE-bridge, the ratio of the resistance of the other to Pt_I was determined by means of the differential galvanometer. Pt_V was also measured separately with the WHEATSTONE-bridge. The difference of the results by the two methods amounted only to 0,02 % at the lowest temperatures.

Just as Pt_I, Pt_{III} and Pt_V were supplied by HERAEUS; they were delivered at the same time, but later than Pt_I. The diameter of all three was 0.1 m.m. After having been treated and wound round the glass (see Comm. N°. 95c § 3) in the same way, they were heated for a long time in an annealing furnace for glass. Pt_{III} and Pt_V differed only in this respect that after being heated Pt_V was partly unwound, and then wound again, and was not heated in the annealing furnace again.

To obtain also a resistance thermometer of very small dimensions a platinum wire of 0,05 m.m. diameter was wound round a tube of 1 c.m. diameter and about 8 c.m. long. The thin platinum wire was welded to thick platinum wires which were fused in the glass. Consequently the thermometer could be cleaned by means of acids if necessary. The thin wire Pt_Δ used for this thermometer, was also furnished by HERAEUS.

A fourth wire was investigated to get an idea of the

§ 3. *Invariability of the resistance thermometers for low temperatures with the time,* viz. the resistance thermometer with which the observations were made by MEILINK in 1902, and which we shall call Pt_M. The zero point appeared to have remained unchanged to one 300000th [1]). This was also the case with Pt_I, after measurements had been made at very low temperatures with the resistance thermometer for two years.

Repetition of the calibration at low temperatures of 1902 did not give an equally good harmony. We found:

[1]) The thermometer had got defect in consequence of the bursting of the glass cylindres. However carefully it was repaired, yet this gave rise to a diminution of length of the wire of 3 mm. or 0,039 %, for which a correction was applied.

TABLE IV.

Hydrogen th.	1902	1907	Deviation in Ω	Deviation in ° C.
0°	110.045	110.048	— 0.003	
—182.63	28.692	28.605	+ 0.087	+ 0°.25
—197.08	21 877	21.999	— 0.022	— 0.05
—209.93	16.025	15.934	+ 0.089	+ 0.25

We think that we cannot draw another conclusion from it than that the reliability of the measurements with the hydrogen thermometer in 1902 was not yet so great as it has become now as appears from Comm. N°. 95d.

§ 4. *Results.* The measurements have yielded for the resistance of each of the wires expressed in that at 0° as unity:

TABLE V. Comparison of different platinum resistance thermometers

Temperature	Pt_I	Pt_{III}	Pt_V	Pt_M	Pt_d
0°	1.	1.	1.	1.	1.
— 30.53	0.87892	0.87846	0.87799		
— 58.58	0.76685	0.76632	0.76643		
— 87.55	0.64991	0.64918	0.65039		
—103.83	0.58345			0.58720	
—109.09	0.56204	0.56025	0.56126		
—140.19	0.43311	0.43195	0.43182		
—159.11	0.35368	0.35240	0.35214	0.35979	
—182.75	0.25283	0.25141	0.25009	0.26022	0.27374
—195.10	0.20045	0.19894	0.19858	0.20812	0.22298
—204.68	0.15974	0.15816	0.15880		0.18355
—212.20	0.12816	0.12653	0.12625	0.13622	0.15285
—216.63	0.11024	0.10853	0.10824		
—252.82	0.01421				0.040637
—255.18	0.01244				0.03766
—259.10	0.01053				0.03645

It appears that wires delivered at the same time show the same course with only small deviations. A considerable difference in deformation of the wire has had only a slight influence for Pt_V. The great difference with wires delivered at different times points to the fact that the originally used material and the treatment in drawing the wires out decide on the change of the resistance. How great the influence of the treatment in drawing is appears from the comparison of P_{III} and Pt_d. They were supplied by HERAEUS about the same time and are therefore probably made of platinum of the same degree of purity. Yet the thinner wire Pt_d decreases much less in resistance than the thicker one. At the temperature of liquid hydrogen the differences become very large. In view of the results obtained for gold, which have been inserted in the following Communication (N°. 99c), the most plausible explanation is this that the admixtures in the platinum of the wires sent by HERAEUS, either due to their being less pure by nature or to the way of drawing, were less with the platinum sent later than with that sent earlier. We come back to this in Comm. N°. 99c. Here we may still mention that DEWAR's wire gave 0,30521 to ours 0,25344 at —182°, and that only the thickest (0,2 m.M.) of HOLBORN's wires gave a smaller value than ours, viz. 0,21253 to ours 0,21786 at —191°.

§ 5. *Calibration formulae for the new wires.* Just as for Pt_I we have also calculated the constants for each of the wires Pt_{III} and Pt_V in a calibration formula which is adjusted down to —217° and does not give to great deviations at the hydrogen temperatures. To be adjusted to the hydrogen temperatures too formulae of another form are required. The above mentioned formulae of the form (*A*):

$$\frac{Wt}{W_0} = 1 + a.t.10^{-2} + b.t.10^{-4} + c.t.10^{-6} + d\left(\frac{10^3}{T} - \frac{10^3}{(273.09)^3}\right)$$

give for the adjustment which we distinguish by A_I:

A_I	*a*	*b*	*c*	*d*
Pt_V	+0.401819	+0.0007403	+0.0052641	+0.020666
Pt_{III}	+0.398291	−0.0026645	+0.0039442	+0.016843

The mean error proved to be greater, for Pt_V even considerably greater than in the calibration in Comm. 95c, which can be ascribed only partly to the indirect method of the determination of the resistance.

Physics. — *"Isotherms of diatomic gases and their binary mixtures. VI. Isotherms of hydrogen between — 104° C. and — 217° C."* (Continued). By Prof. H. KAMERLINGH ONNES and C. BRAAK. Communication N°. 99[a] from the Physical Laboratory at Leiden.

(Communicated in the Meeting of June 29, 1907).

§ 14. *Survey of the determinations.*

The determinations mentioned in this Communication constitute one whole with those of Communication N°. 97[a]. They may partly serve to control the earlier determinations at — 104° and — 136°, which, being the oldest observations, are not quite so reliable as the others. For the determinations of isotherms at lower temperatures they are a valuable supplement for the smaller densities from 70 to 100 times the normal one. With the exception of the isotherm of — 217° the determinations communicated now may also be considered as a whole in themselves. To complete this set of determinations a part of the isotherm mentioned for the density at about 170 times the normal one is still wanting. We hope soon to publish the additional determinations referring to this. To the standard-temperatures at which we determined the isotherms, we have still added — 164° C. From the data mentioned in Comm. N°. 97[a] may be derived (see § 13 of the communication mentioned) that the point where the inclination of the *pv*-curve for exceedingly small densities becomes zero, lies at about this temperature. The purpose of the determinations at — 164° is to determine this point, which we shall call the *Boyle-point*, more definitely.

The determinations, with the exception of that at — 140°, were made at temperatures which differed little from the standard-temperatures of Comm. N°. 97[a]. They may be reduced to these standard-temperatures by a simple correction (See Comm. 97[a] § 6). This reduction has not yet been carried out for the isotherms mentioned below. In Table XIX the temperatures are given at which the measurements were made. They were determined and calculated in exactly the same way as those of Comm. N°. 97[a]; just as to these latter temperatures the correction of Table XVIII Comm. N°. 97[b] is still to be applied to them.

We may still remark about the measurement of the pressure (cf. § 3), that for the lowest pressures a direct connection with the open manometer was required, because the closed auxiliary manometer cannot be used below 20 atms.

§ 15. *Remarks about the manometers and the piezometers.*

When the determinations were finished, the auxiliary manometer

was once more compared with the open standard-manometer. It proved that the normal volume had again undergone a slight diminution, i.e. of 0.00026 of the original value. This comparison was made at about 22, 28 and 55 atmospheres. If the calculations of the pressure are carried out with the corrected normal volume, the remaining differences between the indications of the open and the closed manometer are smaller than $\frac{1}{10000}$ of the total pressure.

The steeltube f_4 with hexagonal portion f_5 on the stem of the piezometer b_5 (cf. fig. 2 Pl. II Comm. N°. 69, for the details at the top of the tube compare fig. 4 ibid f_1, f_2, f_4) was soldered to the glass stem b_6 in the way described in Comm. N°. 94^b. Now the packing could be pressed down more tightly (cf. § 4 Comm. N°. 97^a) without danger of the block sliding from the stem.

The dimensions of the different parts of the piezometer were about the same as in the determinations of series I of Comm. N°. 97^a. The glass stem had a greater length and a volume of about 12 cm^3., which enabled us to determine a greater part of the isotherms than was possible in series I. The reservoir had the somewhat smaller volume of 5.1583 cm^3.

§ 16. *Second group of values of* pv_A.

In table XIX the results of the determinations have been given in the same way as in Table XII of Comm. N°. 97^a.

In conclusion we express our hearty thanks to Mr. J. Clay for his valuable assistance in this investigation.

TABLE XIX. H_2. Series IV. Values of pv_A.

N°.	t	p	pv_A	d_A
1	—103°.71	28.423	0.63208	44.967
2		38.154	0.63648	59.944
3		48.682	0.64143	75.897
4		58.317	0.64638	90.222
5	—139°.88	25.432	0.49452	51.428
6		33.774	0.49697	67.960
7		41.273	0.49967	82.600
8		48.558	0.50232	96.667
9		25.380	0.49466	51.308
10	—164°.14	22.818	0.40065	56.952
11		28.688	0.40164	71.427
12		34.387	0.40253	85.427
13		39.947	0.40376	98.936
14	—183°.18	20.409	0.32562	62.677
15		24.705	0.32550	75.898
16		28.374	0.32521	87.248
17		32.416	0.32522	99.673
18		20.400	0.32557	62.663
19	—195°.17	18.554	0.27867	66.581
20		23.337	0.27765	84.055
21		27.879	0.27622	100.933
22	—204°.69	16.752	0.24040	69.684
23		20.456	0.23880	85.658
24		24.019	0.23695	101.367
25	—212°.82	15.416	0.20644	74.679
26		18.038	0.20430	88.296
27		20.643	0.20228	102.051
28	—217°.40	14.638	0.18742	78.103
29		16.787	0.18495	90.766
30		18.857	0.18293	103.080

Physics. — *"On the change of the resistance of the metals at very low temperatures and the influence exerted on it by small amounts of admixtures"* I. By Prof. H. KAMERLINGH ONNES and J. CLAY. Communication N°. 99[c] from the Physical Laboratory at Leiden.

(Communicated in the meeting of June 29, 1907).

§ 1. *Introduction.* In Comm. N°. 99[b] we called attention to the very large differences in the change of the galvanic resistance with the temperature, which different platinum wires show when we descend to the low temperatures which are to be reached with liquid hydrogen. Such differences were still more pronounced for different gold wires which we investigated. With this metal (see Comm. N°. 95[d] These Proc. Sept. 1906) we had taken in hand the investigation of the influence of small amounts of admixture announced in Comm. N°. 77, because the influence of admixing silver would probably be important and the percentage of silver could be determined very accurately, the possibility of drawing out wires of the different kinds of gold and its high melting point moreover rendering this metal preferable to the for the rest very suitable mercury.

Besides, the inquiry into the influence of small amounts of admixture on the change of the resistance of gold with the temperature proved at once useful as we thought that the gold resistance thermometer would be preferable to the platinum resistance thermometer. Dr. C. HOITSEMA, who already obliged us before (see Comm. N°. 95[d]) by putting pure gold at our disposal, has had the kindness of supplying us again with different samples of gold of high purity, further of preparing for us different alloys with accurately known small percentages of admixture, and of determining the impurity which was finally left in the wires after they had been melted down. For all this valuable help and for the information which Mr. HOITSEMA was enabled to give us by his wide experience we express our hearty thanks.

The investigation of the different gold wires with very small amounts of admixture may of course also be considered as the calibration of different gold resistance thermometers. (Comp. Comm. N°. 99[b] § 1). We prefer, however, to consider it as a part of our more general investigation (Comm. N°. 77) on the change of the resistance with the temperature for pure metals, and on the influence which small amounts of admixture exert on it.

As to the change of the specific resistance for the pure metals reduced to the most normal state, attention is drawn to the temperature of the

point of inflection $\frac{d^2r}{dT^2} = 0$ the temperature of the *point of proportionality* $\frac{dr}{dT} = \frac{r}{T}$ and the temperature of the *minimum* $\frac{dr}{dT} = 0$. It is clear that the situation of these points, and the correspondence[1]) and difference of their situation and of the coefficient of variability of the resistance with the temperature in general for different metals of different classes must furnish important data for the theory of electrons.

The investigation of these points is only possible by the aid of liquid hydrogen. Only in some cases — and even then the purity of the metal is open to doubt — the point of inflection, whose existence was indicated by DEWAR, was found high enough to be ascertained without measurements for hydrogen temperatures. For metals in the purest and normal state the point of proportionality lies probably still below the temperatures which are to be reached with liquid hydrogen. It is true that DEWAR derived from his measurements at two hydrogen temperatures that it was surpassed for some of his metal wires. Our measurements, however, point to this that as a metal is brought to a purer and more normal state, the point of proportionality is found to be lower. The metal wire which came nearest to this *ideal* state, was one of our gold wires. Even at the lowest temperature the point of proportionality was not yet reached for that wire. Probably DEWAR'S wires were further removed from this ideal state.

With the low situation which we find for the point of proportionality measurements at two hydrogen temperatures do not suffice, but we have made determinations at at least three hydrogen temperatures, because they were necessary to determine the probable situation of the point of proportionality by the aid of $\frac{d^2r}{dt^2}$. Until we have reached the proportional point, we need not discuss the question of the minimum point.

In the inquiry into the properties of the metals in the ideal state we must know first of all in how far the metal is in this state, and else how we can derive what would be found in this state. The influence of small deviations in the nature of the metals on the change of the resistance with the temperature, becomes so exceedingly great for the hydrogen temperatures, that a special investigation is necessary for them. Here two things have to be paid attention to: to small amounts of admixture, and to differences in

---

[1]) In this respect something is to be derived from the formulae given by us in this and in the preceding communications.

hardness etc. For the present we have left the latter out of account; in the investigation of the influence of the admixtures, however, the influence of the hardness was as much as possible eliminated by our treating the different samples of metals exactly in the same way when comparing them, and by reducing them to the same state of softness.

The most natural explanation of the whole of the results obtained as yet (in this and the preceding Communication) is to ascribe the deviations for the different wires of one and the same metal to impurities in the metal, which may also come in during the drawing if efficient precautions do not prevent it, and which even in very small quantities exert a very great influence on the changes of the resistance with the temperature.

The influence of the drawing is altogether lost for mercury, in which it is also easy to ensure uniform distribution of small quantities of admixture. This enhances the importance of the study of this metal for the investigation of the influence of admixture. In the first place we have measured its resistance at hydrogen temperatures which had not yet been determined; it is given in § 4. It proved that for pure mercury [1]) the inflection point falls in the region of liquid hydrogen temperatures. This is a drawback for the inquiry into the change of the resistance with the temperature for pure metals.

Just as the gold wire Au_V (see § 2), also the silver wire Ag_I and the platinum wires of the preceding Communication are probably purer than DEWAR's wires of the same metals. For bismuth, on the other hand, DEWAR has most likely had a purer sample than we. The change of the resistance at hydrogen temperatures for this metal, which had not yet been measured by him, has been given in § 5. The observations for lead for those temperatures, which were still wanting up to now, have been given in § 6.

The high degree of purity for some of the metals which were at our disposal, and the lower temperatures to which we descended (solid hydrogen evaporating at 2,5 m.m. pressure) render the decrease of the resistance in some cases many times larger than was observed by DEWAR. To this it is also owing that we have observed the great influence, which very small changes in the nature of the metal obtain on the change of the resistance at hydrogen temperatures. We may account for this by paying attention to the difference of the resistance of a wire of pure metal at the temperature T, r_{iT}, with

---

[1]) Perhaps in connection with the low melting point. Possibly the point of proportionality is first reached for osmium.

that of a wire of the same metal with a proportion of admixture x at the same temperature, r_{xT}. According to a theorem of MATTHIESSEN [1]) derived from observations between 0° and 100°, this difference (the theorem refers to a difference that is about the same as that considered here) is constant for different temperatures. FLEMING [2]) found this theorem about confirmed down to — 200°. As we have found, this theorem no longer holds for hydrogen temperatures. But the deviation is not of such a nature as to affect our conclusions. So if to form an idea of the influence of the admixtures, we put $r_T = r_{iT} + px$, further p constant and large, then it is clear that — when r_{iT} becomes as small as is the case (see Table I Au_V) for pure metals and hydrogen temperatures — the resistance of a metal for the case that x gets an appreciable amount, will be owing almost exclusively to the admixture. The small amounts of admixture obtain a remarkable influence [3]).

Analogues are easily found in the important influence of small amounts of admixture on the density in the neighbourhood of the critical temperature of a substance, in a space becoming opaque by a cloud depositing on a minimum quantity of dust. But for a further discussion the systematic investigation of the influence of small amounts of admixture should be more advanced. At all events the changes of the resistance with temperature at hydrogen temperatures proves to be a highly sensitive criterion to decide about the nature of a metal.

§ 2. *Gold.* The different samples of pure gold were all supplied by Dr. C. HOITSEMA. With the exception of two the wires were all treated in exactly the same way, drawn out by HERAEUS to 0,1 mm. diameter, and treated at every pull with diluted sulphuric acid and nitric acid. The gold wire Au_{VI} was drawn in a different way and made strongly impure. The exact amount has not yet been ascertained.

---

[1]) Pogg. Ann. Bd. CXXII.

[2]) Proc. Royal Institution June 1896 p. 9.

[3]) To a less degree of purity of the examined metal wires it is perhaps to be ascribed that NICCOLAI, Att. Linc. 16, 1st sem. p. 906 finds a smaller decrease of resistance at — 189° than we do, as appears by comparison with Tables I, III, V of this communication and V of Comm. N°. 96*b*. Indeed NICCOLAI finds:

	silver	gold	lead	platinum
0°	1	1	1	1
— 189°	0.2784	0.3068	0.3357	0.3198

[Added in the translation].

Au_0 is the wire which was calibrated in Comm. N°. 95^d. After melting it down Dr. HOITSEMA found 0,03% impurities. As to the wires Au_{III}, Au_{IV} and Au_V, Dr. HOITSEMA found about 0.015% admixture for Au_{III}, about 0.005% admixture for Au_{IV} and Au_V. $Au_{Ag\,I}$ was made of an alloy which after the wire had been remelted, contained 0.4 % admixture (probably chiefly silver). Wound round the same glass cylinder all wires except Au_0 and $Au_{Ag\,I}$ were heated at the same time in an annealing furnace for a long time, and slowly cooled, as had also been done with Au_0 and $Au_{Ag\,I}$, so that they were perfectly malleable.

In table I the resistances have been given expressed in that at 0° as unity. These were about 9Ω.

TABLE I.

Change of the resistance of different gold wires with the temperature.

Temperature	Au_{III}	Au_{IV}	Au_V	Au_{VI}	Au_0	$Au_{Ag\,I}$
0°	1	1	1	1	1	1
—103.83	0.59601	0.59389	0.59306	0.64827	0.60545	0.64549
—183.00	0.27653	0.27177	0.27096	0.37053	0.30070	0.37099
—197.87	0.21456	0.20963	0.20871	0.31659	0.23908	
—205.01			0.17897		0.20992	
—215.34	0.14058	0.13407	0.13337	0.16822	0.16681	
—252.93	0.01602	0.008743	0.008103	0.13669	0.04554	0.13942
—255.13			0.005691			
—258.81	0.01095	0.004265	0.003601	0.13241	0.03982	0.13288
[—261]			0.002713			
[—262]		0.003257	0.002526			

To facilitate comparison we may observe that DEWAR found 0.03290, whereas we found 0.008103 at — 252°.93 for Au_V.

§ 3. *Mercury.* It was doubly distilled and brought into a glass spiral. The latter was protected by a bath of pentane, which was slowly cooled from the bottom upwards before it was immersed into the bath of the cryostat. We found:

TABLE II.

Change of the resistance of pure mercury with the temperature

Temp.	Resistance
0°	97.126
— 183.00	7.2650
— 197.87	6.0103
— 205.01	5 3900
— 215.34	4.5057
— 252.93	1.2613
— 258.81	0.7534

§ 4. *Silver*. This was also supplied by Dr. C. HOITSEMA and drawn to a wire of 0.1 m.m. by HERAEUS, during which operation it was treated in exactly the same way as the gold and the platinum. After the resistance had been determined, the composition was controlled; the silver contained then 0.18% impurity. The zero point

TABLE III.

Change of t e resistance of silver with the temperature.

Temperature	Resistance Ag_I	$O-C_D$	$O-C_{A_{IV}}$
99°.76	1.41089	0	0
0 before	1	0	0
0 after	1.00037		
— 103.81	0.58087	— 0.00042	— 0.00042
— 139.87	0.43282	+ 42	+ 42
— 183.57	0 24679	— 17	0
— 195.17	0.19703	+ 29	— 2
— 204.67	0.15528	— 31	
— 252.92	0.008913	0	
— 259.22	0.006 42	0	

of the silver wire (resistance at 0°) changes slightly by being drawn out in consequence of the difference in expansion of silver and glass. The preceding table gives the resistance expressed in that at 0° as unity. (The resistance at 0° was 21.519 Ω).

Column $O—C_D$ contains the deviations from a formula adjusted from + 100° to — 259° of the new form:

$$\frac{W_t}{W_0} = 1 + a \,.\, 10^{-2} \,.\, t + b\, 10^{-4}\, t^2 + c\, 10^{-6}\, t^3 + d\left(\frac{10^6}{T^3} - \frac{10^6}{(273.09)^3}\right) + e\left(\frac{10^{10}}{T^5} - \frac{10^{10}}{(273.09)^5}\right) \quad . (D)$$

which agreed best with the values:

D	a	b	c	d	e
Ag_I	+0.402746	+0.004355	+0.004806	+0.00955	—0.000013

For a comparison with platinum and gold the column $O—C_{A_{IV}}$ gives the deviations from a formula of the form A (see Comm. N°. 95^c and 95^d):

$$\frac{W_t}{W^0} = 1 + a.t.10^{-2} + b.t^2.10^{-4} + c.t^3.10^{-6} + d\left(\frac{10^3}{T} - \frac{10^3}{273.09}\right)$$

with values which we distinguish by A_{IV} on account of the other way of adjusting the coefficients.

A_{IV}	a	b	c	d
Ag_I	+0.40355	+0.03968	+0.005232	+0.008662

§ 5. *Bismuth.* The measured resistance, which we shall also investigate in the magnetic field, was that of a bismuth spiral of HARTMAN and BRAUN N°. 301. The resistance expressed in that at 0° as unity (the resistance at 0° was 17.3138 Ω) was:

TABLE IV.

Change of the resistance of Bismuth with the temperature.

Temperature	Resist nce Bi_I	$O-C_{A_{III}}$
12°64	1.05148	0
12°70	1.05165	
0	1	
— 103.71	0.63649	+ 0.00952
— 139.88	0.52865	— 127
— 164.05	0 46246	— 144
— 182.73	0 41435	— 69
— 195.17	0.38478	+ 144
— 204.68	0.36064	+ 127
— 216.01	0.33014	— 69
— 253.01	0.22329	— 92
— 255.34	0.21388	— 2
— 258.86	0.19574	0

This column $O-C_{A_{III}}$ gives the differences with a formula of the form A (see § 4), with values which we shall indicate by A_{III} on account of the adjustment at two hydrogen temperatures and over the region to 0°:

A_{III}	a	b	c	d
Bi_I	+0.399037	+0.051928	+0.0038155	—0.0079700

§ 6. *Lead.* The knowledge of the resistance of lead is of particular importance on account of the fact that this metal does not show the THOMSON-effect. Probably the lead used by us, contained no more than 0,015 % admixture.

The resistance of a narrow strip cut out from the flatted lead and protected against chemical action by paraffine expressed in the resistance at 0° (3.18114 Ω) as unity was found to be:

TABLE V.

Change of the resistance of lead with the temperature.

Temperature	Resistance
+ 16°.33	1.0652
0°	1
—103.63	0.59548
—183.65	0.29439
—195.15	0.25257
—204.52	0.21742
—216.61	0.17129
—252.78	0.03039
—255.07	0.02314
—258.70	0.01311

Physics. — *Repetition of* DE HEEN'S *and* TEICHNER'S *experiments on the critical state*", by Prof. H. KAMERLINGH ONNES and G. H. FABIUS. Communication N°. 98 from the Physical Laboratory at Leiden.

(Communicated in the meeting of April 26, 1907).

§ 1. *Introduction.* Experiments have been repeatedly made from which the conclusion was drawn, that a substance can assume different densities above its critical temperature with the same pressure and the same temperature, which densities it can retain for hours according to some investigators [1]). That in reality this is not the case, and that the

[1]) TRAUBE Ztschr. f. phys. Chem. 58 p. 477. 1907, cf. also MATHIAS, Le point critique des corps purs p. 250.

When with change of density dissociations or variations of volume of the molecules themselves should made their appearance which clearly require more time than the establishment of temperature equilibrium through conduction of heat and convection, we should when a phase was kept at constant volume after having suffered variation of density, have to find an increase of the pressure both for liquid and vapour phases and for phases above the critical temperature; thermodynamically it follows from this that the density of liquid in equilibrium with vapour would then have to be a function of the time.

Cf. TRAVERS and USHER on variations of density in consequence of false equilibria.

differences found are to be ascribed to admixtures or to differences in the pressure or the temperature of the phases compared appeared already when KUENEN (Comm. n°. 11, Verslag Kon. Ak. v. Wet. May and June 1894) repeated GALITZINE's experiments (Wied. Ann. 50, 1893), and found but trifling differences remaining. Afterwards when DE HEEN (Bull. Ac. Belg. 3e S. t. XXXI '96) had again found the differences of density in question by another way, it was shown by repetition of his experiments at Leiden (Comm. N°. 68, These Proc. April 1901 p. 628 and p. 691), that also these differences of density vanish almost entirely for pure CO_2 when attention is paid to the differences of temperature. In the last few years, however, it has been particularly TEICHNER's [1]) experiments that have given new support to the opinion that after all these differences of density really exist (Drudes Ann. 13, 1904).

In the first place we have repeated DE HEEN's experiment in different ways. Already with the earlier repetition (1901) thermo-elements had been introduced for the determination of the difference in temperature of the two metal reservoirs of the apparatus, which were separated by a cock, the apparatus for the rest resembling that of DE HEEN as closely as possible. One of the thermo-elements, however, was damaged during the experiments. Though it could be ascertained that the differences in density even without correction for the temperature were considerably smaller than those found by DE HEEN, probably on account of the greater purity of the CO_2, the exact amount of the difference remaining after temperature correction could not be determined. To replace these measurements by better ones a new, improved apparatus with thermo-elements was built, resembling for the rest DE HEEN's apparatus as closely as possible, and with this apparatus we made the observations communicated in § 3. They confirm that the differences in density derived by DE HEEN from his experiments do not exist for a pure substance when temperature and pressure are uniform [2]).

---

[1]) In the TEICHNER's tube the same differences of density which GALITZINE and WILIP (Congr. Intern. de Physique I 668, 1900) had found were shown by GILBERT-FARADAY's density-bulbs. What holds for TEICHNER's experiments applies therefore also to those of GALITZINE and WILIP.

[2]) So if there exist processes as meant in p. 215 note 1, they pass so quickly that it is not possible to demonstrate them by methods which require that the equilibrium of pressure and temperature has first been established. As yet nothing has been found that points to the fact that the establishment of the temperature equilibrium is retarded an appreciable time on account of changes of energy which increase in course of time to a definite limiting value, the volume remaining constant. It was demonstrated in Comm. N°. 68 that admixtures and differences of tem-

Further we have repeated TEICHNER's experiment [1]) with more precautions than had been taken by this observer. Especially a thermoelement (platinum-platinum-iridium not to sacrifice the security which the glass apparatus offers for the preservation of the purity of the substance) was adjusted in the upper and in the lower end of the TEICHNER tube, just as in DE HEEN's modified apparatus, to enable us to follow the differences of temperature in the tube.[2]) By using CO_2 for the experiment, a high degree of purity could be reached, and we came into a region where the temperature could be kept constant up to a very small amount.

If we wish to prevent diffusion between the higher phases and the lower ones, the modified TEICHNER tube (at least when not a capillary constriction has been made in it [3]) is inferior to the modified apparatus of DE HEEN. Moreover when we wish to reach the equilibrium of temperature quickly, the bad conductivity of heat of the glass is a drawback, but it has the great advantage, that the changes of density can be observed at the same time with the other phenomena for the critical state. With regard to these phenomena TRAVERS and USHER (Ztschr. f. phys. Chem. 57, p. 365, 1906) and YOUNG (ibid p. 262) published important papers, after we had made the experiments mentioned in § 7. In the main points our observations agree with the descriptions given by TRAVERS and

---

perature lead to systematic disturbances as in DE HEEN's experiments. Both give rise to disturbances of the same character. In the discussion of the influence of the differences of temperature the valuable paper by VILLARD Ann. d. Ch. et d. Phys (7) 10. 1897 has been overlooked there. That TEICHNER's results might be ascribed to small admixtures has appeared in details from the calculations by VERSCHAFFELT (Comm. Suppl. n°. 10, (Dec. 1904).

To the influence of admixtures on phenomena in the neighbourhood of the critical point attention has also been drawn by YOUNG Journ. de Chim. Phys. 4 (1906) p. 475. To this may be added that KEESOM, Comm. No. 88, These Proc. Jan. 1904 p. 593 did not only consider the increase of the pressure during condensation with constant temperature as a proof of the presence of admixtures, but that it served him further to arrive at an opinion on the quantity of the admixture.

1) This was already mentioned Comm. Suppl. No. 10 These Proc. Dec. 1904. Lately TRAUBE strongly urged the advisability of a repetition.

2) In a CAGNIARD-LATOUR tube thermometers were fused by VILLARD. Our tube may just as well be called a VILLARD tube with density-bulbs as a TEICHNER tube with thermo-elements.

3) Such an apparatus, if necessary provided with a valve which is worked magnetically might be serviceable in the investigation of the variation of density with temperature. [After this was printed we noticed that the device of a capillary constriction was used by RAMSAY, Proc. Roy. Soc. 30 (1880) p. 327. Note added in the translation].

USHER and by YOUNG, and supplement them by giving the variations of the densities.

After what the repetitions of DE HEEN's experiments had taught us again about the asserted differences of density at the same pressure and the same temperature above the critical temperature, our repetition of TEICHNER's experiments has become rather a first contribution to the study of the variations of density with temperature and pressure by this way, than a refutation of the conclusions derived from TEICHNER's experiments. We have, however, been able to show sufficiently by our experiments that these conclusions are erroneous.

§ 2. *Repetition of one of* DE HEEN's *experiments.* As we can refer to Comm. n°. 68 with regard to the choice of the experiment which is to be repeated (on account of the systematic character of the deviations only one need be repeated), and as on another occasion a full description of the apparatus used and the different operations will be given, we think that the following remarks on the arrangement of the experiments will suffice here.

1. The pure carbonic acid was prepared by distillation. The admixtures are to be estimated at no more than 0,00027 (cf. KEESOM Comm. N°. 88 II, § 2 and V § 10 These Proc. Jan. 1904). In the apparatus it comes into contact only with metal, glass, and cork (packings of this gave a perfect closure after having been repeatedly tightened during a week.).

2. The apparatus, the conduits, and the further auxiliary arrangements, among which also two metal bottles with the purified CO_2, are all in connection with a mercury airpump. One of the bottles with pure CO_2 serves for rinsing. From the second the desired quantity is conveyed into the apparatus by distillation.

3. The density in every reservoir is determined by making the carbonic acid flow from it into a large reservoir with mercury manometer kept at constant temperature. In the volumenometric calculations the corrections are applied according to the empiric equation of state V s. 1 of Comm. n°. 74 (Arch. Néerl. (2) 6, 1901). Errors in the density caused by leakages in the reservoirs at high pressure are excluded. It was ascertained by separate control experiments that the total amount of CO_2 in the apparatus remained unchanged during the experiments.

4. The apparatus was kept at uniform constant temperature by means of flowing water, a xylene thermoregulator (see Comm. N°. 70 III § 3 These Proc. May 1901) and a valve stirrer (see Comm.

N°. 83 III § 4 These Proc. Febr. 1903). Sufficient precautions were taken to prevent conduction of heat from outside to parts of the apparatus.

§ 3. *Variations of density found in the repetition of the experiment of* DE HEEN *after correction of the difference in temperature of the reservoirs.*

DE HEEN brings the temperature of the two reservoirs (see § 2 beginning) from 28° to about 35° C, and opens the cock between them 6 times four seconds during the heating; then when the temperature has become constant at about 35°, he opens the cock once more 6 times 4 seconds. Then he assumes that temperature and pressure are the same in the two reservoirs.

When repeating the experiment (being very careful to prevent drops from being scattered from one reservoir into the other) we found confirmed by reading the thermo-elements (nickel-iron), what was observed in Comm. N°. 68 viz. that every time when the cock between is opened for adjustment of pressure, a difference of temperature arises between the two reservoirs, and that when closing the cock at the end of the experiment a difference of temperature remains, which must be taken into account.

In order to find out in how far the equilibrium of temperature and pressure has been reached, we have in the first place made three determinations, in which the cock was opened respectively 2, 4, and 6 seconds every time (probably our cock allowed comparatively less substance to pass than that of DE HEEN). The results have been given in the following table: v denotes the upper, l the lower reservoir, so ϱ_l is the density in the lower reservoir; the numbers of times the cock was opened during the heating (distributed over 15 minutes) and then at constant temperature (distributed over half an hour) have been separately given; ϱ'_l is ϱ_l corrected for $t_v - t_l$.

SERIES I.

Establishment of the equilibrium by opening the cock	ρ_v	ρ_l	ρ_l/ρ_v	t_v	$t_v - t_l$	Corrected for difference of temperature	
						ρ'_l	ρ'_l/ρ_v
6 times 2 + 6 times 2 sec.	0.418	0.506	1.21	34°.25	0°.27	0.456	1.09
6 times 4 + 6 times 4 sec.	0.424	0.495	1.17	34.40	0.22	0.454	1.08
6 times 6 + 6 times 6 sec.	0.427	0.489	1.15	34.20	0.16	0.456	1.07
6 times 6 + 6 times 6 sec.	0.437	0.501	1.15	34.30	0.20	0.466	1.07

The temperature corrections have been borrowed from the graphical representation derived in Comm. N°. 68 from AMAGAT's determinations. The uncertainty which still prevails with respect to the correct course of the isotherms in the neighbourhood of the critical state is, of course, also found in these corrections.

The rather rapid process of the heating from 28° to 35° prevents further that the whole apparatus has already assumed the temperature of the waterbath, so that also the observed differences of temperature themselves are not quite certain.

In the following series of determinations we proceeded in the same way till the 12th opening (the 6th at constant temperature). It was put off for 3 hours. When the cock was opened the course of the deviations of the galvanometer appeared to be the same as in the preceding series; the remaining temperature corrections, however, were somewhat smaller than in the 1st series, which we ascribe to this that all parts of the apparatus have had time to assume the temperature of the waterbath. An increase of pressure in the lower reservoir, which should have been found when e. g. in this lower reservoir molecules were dissociated during these three hours (see § 1, p. 216 footnote 2), and which should have given rise to a greater galvanometer deviation when the cock was opened for the last time, could not be traced. We found:

SERIES II.

Establishment of the equilibrium by opening the cock	ρ_v	ρ_l	ρ_l/ρ_v	t_v	$t_v - t_l$	Corrected for difference of temperature	
						ρ'_l	ρ'_l/ρ_v
6 + 5 + 1 time 2 sec.	0.430	0.497	1.16	34°.55	0°.20	0.466	1.08
6 + 5 + 1 „ 4 sec.	0.440	0.489	1.11	34.85	0.16	0.456	1.04
6 + 5 + 1 „ 6 sec.	0.439	0.485	1.10	34.40	0.15	0.452	1.03

In virtue of what the preceding determinations had taught us as to the reaching of equilibrium of temperature and pressure the cock was opened 12 times 12 seconds in a following determination, and finally two more determinations were made in which the cock was opened 12 times 4 seconds and at last once five minutes. We found:

SERIES III.

Establishment of the equilibrium by opening the cock	ρ_v	ρ_l	ρ_l/ρ_v	t_v	$t_v - t_l$	Corrected for differences of the temperature	
						ρ'_l	ρ'_l/ρ_v
6 + 6 times 12 seconds	0.446	0.488	1.09	34.70	0°.20	0.456	1.02
6 + 6 times 4 sec.	0.427	0.445	1.04	34.05	0.06	0.432	1.01
at last 5 minutes	0.462	0.478	1.03	34.00	0.06	0.467	1.01

From this follows that as the equilibrium of pressure and temperature is obtained better, the densities of the phases become more and more equal, and that at last after the application of the temperature correction only very small differences remain.

The much more considerable deviations found by DE HEEN ($\varrho_l/\varrho_v = 1.19$, see Comm. No. 68) must, therefore, be attributed to admixtures and differences of temperature. [1] [2]).

§ 4. *Example of differences of density as found by* DE HEEN, *caused by a slight impurity of the* CO_2.

The great influence of small quantities of admixture is very convincingly shown by the following results.

In a group of determinations ending with a repetition of experiment 2 Series I we found:

Establishment of the equilibrium by opening the cock	ρ_v	ρ_l	ρ_l/ρ_v
6+6 times 4 sec.	0.392	0.531	1.35

It appeared that in consequence of carelessness in the cleaning after it had been repaired, in the metal bottle in which the pure

[1]) That during the opening of the cock no important exchange of liquidogeneous and gasogeneous molecules between the upper and the lower reservoir can have taken place (to use the terminology of DE HEEN), appears from this, that when the upper reservoir was filled with air and the lower reservoir with air with 31 pCt. CO_2, and the equilibrium was established without the cock being opened, after the cock had been opened for 5 minutes, only 0,33 percent of $C\Theta_2$ had passed into the upper reservoir.

[2]) They give both systematic errors of the same character (cf. § 1 p. 2 note 1 above).

carbonic acid was kept, a trace of oil had been left which had diffused in the carbonic acid. When we thought that the whole apparatus had been sufficiently cleaned by blowing pure carbonic acid through it, we found:

Establishment of the equilibrium by opening the cock	ρ_v	ρ_l	ρ_l/ρ_v
Only 6 times 4 sec. during the rise of the temperature.	0.385	0.555	
6 + 3 times 4 sec.	0 399	0.521	1.30
6 + 6 times 4 sec.	0.417	0.505	1.21

which by the side of Series I and II gives at the same time an idea with what degree of approximation equilibrium of pressure is reached by the repeated opening of the cock. Repeating the last determination after continued blowing we found:

6 + 6 times 4 sec. | 0.426 | 0.496 | 1.19

The last observation harmonizes pretty well with Series 1 N°. 2, of which it is a repetition, the same deflections of the galvanometer being moreover found. It leads to the same ϱ'_l/ϱ_v.

It appears how misleading even the presence of slight impurities may be, and that in Comm. N°. 68 the leather packings have been justly called a fundamental defect of DE HEEN's apparatus (cf. 1 § 2 above).

§ 5 *Correction for gravity and for slight admixtures in the experiment of* DE HEEN. *Result.*

In order to be able to calculate the correction which is to be applied to ϱ'_l/ϱ_v for gravity, we must know the density as function of the level in a column of pure CO_2. The accurate shape of the isotherms in the critical state being very uncertain [1]), this function is not accurately known. GOUY has taken SARRAU's equation of state as basis for his calculation. We have started from the equation of state V s. 1 of Comm. N°. 74. Only 0,0002 was found for the correction at 34° and 8 c.M. difference of level, so that it may be neglected. As to the correction for the admixtures for the CO_2, when we put their amount as given in § 2, at 0,00027, it becomes

[1]) It is just to the knowledge of this shape that observations as made in § 3 and § 7 may contribute.

1 % à 1,5 % at 34°.5 according to the calculations of VERSCHAFFELT, Comm. Suppl. N°. 10. If the uncertainty of this correction is taken into account, we must come to the conclusion, the limit of accuracy of our experiments not being higher than 1 % either, that the differences of density derived by DE HEEN from his experiments do not exist for pure CO_2 when sufficient care is taken to ensure equilibrium of pressure and temperature.

§ 6. *Repetition of* TEICHNER's *experiment.* An elaborate description of the apparatus and the operations will be given on another occasion. Here the following remarks may suffice:

1. Repetition with CO_2 was considered to be desirable also by TEICHNER because it gives more warrants for purity.

2. A platinum-platinum-iridium thermo-element (used with a magnetically protected galvanometer of DUBOIS) was successfully fused into TEICHNER's tube at the top and at the lower end, so that the tube remained proof against a pressure of 150 atmospheres. However we did not succeed in making the thermo-elements free from disturbing electromotive forces, nor did they give with certainty the accuracy of 0°.01 we wished. The places of contact were found at $^1/_4$ and $^3/_4$ of the height of the tube. A third thermo-element to compare the temperature in the tube with that in the bath would be desirable.

3. The critical density of CO_2, 0.469 [1]), being smaller than that of CCl_4, with which substance TEICHNER worked, it was much more difficult to obtain the required density-bulbs (small glass bulbs) of 0.365, 0.390 and 0.405. We owe them as well as the fusion of the thermo-elements to the skill of Mr. O. KESSELRING, chief of the glass-blowing department of the laboratory. By means of CLEBSCH's formula it was found that the decrease of volume of the bulbs at the highest pressures can only amount to from $^1/_{600}$ to $^1/_{400}$.

4. Still greater care was devoted to the purification of the CO_2 than in the repetition of DE HEEN's experiment. From a metal bottle of CO_2 as used for the latter, $^1/_3$ is once more blown off, and then $^1/_3$ distilled over into a second bottle from which under weighing, so much is suffered to escape that a fixed quantity remains. This second bottle is connected by glass tubes with the experimental tube, a mercury manometer, a mercury airpump and an auxiliary bottle (also of metal) with pure CO_2 for rinsing the conduits, after which the fixed quantity which it contains, is quite distilled over into the

[1]) Derived by KEESOM Comm. N°. 88 These Proc. Jan. 1904, p. 574, from his observations by means of the rule of the rectilinear diameter.

experimental tube, the latter being immersed in liquid air; at last the experimental tube, still immersed in liquid air, is connected with the mercury airpump, and fused off. By weighing it is ascertained that the desired quantity has been transferred to the experimental tube.

5. A mode of heating which does not give rise to convection currents inside the tube, is considered of great importance also by TEICHNER and TRAUBE, to prevent mixing of what is at the upper end and what is at the lower end of the tube. TEICHNER does not accept YOUNG's refutation of his experiments (see TEICHNER, loc. cit.) because in YOUNG's apparatus convection currents are not so well prevented as in that of himself. The thermostat used by us, however, satisfies much higher demands than that of TEICHNER. The tube is immersed in a liquid bath in a double walled non-silvered vacuum-glass which is hermetically closed with a badly conducting lid. The glass is provided with a valve-stirrer and an arrangement to heat the bath electrically from above, and is itself again immersed in a bath with double glass walls, which is likewise provided with a valve-stirrer. With the exception of two windows, the space between these two walls is filled with cotton wool, by which the outer wall too is surrounded. Like the bath in which the improved apparatus of DE HEEN (§ 2) was placed, the outer bath was kept at constant temperature (up to 0°,02) by flowing water with the aid of a xylene thermoregulator (§ 2). In this way the temperature of the bath in which the experimentaltube is, can be kept constant up to 0°,002. The heating takes place according to the indication of thermometers divided into 50th of a degree, which are placed in the inner and in the outer bath, and is regulated in such a way that everything that might give rise to convection currents is as much as possible avoided.

6. When manipulated the tube was always efficiently shielded for the protection of the observer.

§ 7. *Observations.* The bulbs correspond with the densities 0.365, 0.390, 0.405, 0.421, 0.443, 0.450, 0.466, 0.483, and 0.510.

The position of the bulbs and that of the meniscus (indicated in what follows by the read number of the mark of division between [ ]) was read on a millimeter scale etched on the tube; in the middle of the tube the mark 30 is found, the zero point is 20 mm. above the bottom.

In the *first experiment* the heating took place very slowly; at first also the inner bath was (electrically) heated, t refers to the outer bath, t_i to the inner one. After three hours small gas bubbles were seen to rise from the downmost thermo-element, probably

caused by conduction of heat along the threads, in consequence of t_e having increased too much. We observed:

June 29 1906.

time	t_e	t_i	men.	
11^h	27°.8	27°.15	[31]	
11 30		27.92		
12 20		30.00		
12 25	30.4	30.39		the rising of the gas bubbles has finished, the bulbs begin to show a tendency to divide
12 30		30.69		0.365 rises
12 33		30.83		0.365 at 33
12 36		30.88	[33]	0.510 begins to descend slowly to 25
		30.94		0.510 at 5
		30.99		0.510 on the bottom
				the separate (electrical) heating of the inner bath is stopped,
12 40	31.00	31.00		0.365 at 36
				0.483 begins to descend
12 44		31.00	[34]	0.365 between 38 and 39
				0.483 „ 21 and 22
				t_i rises very slowly whereas t_e was all the time kept somewhat higher to $2^h.50$
12 48				0.483 between 10 and 11
				0.365 rises to the top with accelerated motion
				0.483 continues to descend very slowly
12 52			[34.5]	0.483 has arrived at the bottom all except 0.510, 0.483, and 0.365 in meniscus
1			[35]	0.390 begins to rise
1 3				0.390 between 37 and 38 with 0.405 by its side somewhat lower
1 10				0.390 between 38 and 39 with 0.421 below it in a slanting direction
1 15			[35]	0.421 begins to rise, for the rest like $1^h10'$.

Looking from the top downward in a slanting direction through the tube we observe a slight grey mist which is denser in the part below the meniscus. When we look straight through the tube, with a light behind the tube, the whole shows a light brown colour, which is somewhat darker under the meniscus.

The bulbs continue to move slowly apart, the rising ones

moving faster than the descending ones, and the velocity of the rising bulbs increasing as they get higher, the same thing taking place though in a smaller degree with the descending ones.

2^h15 31.032 the meniscus has gradually got fainter and is hardly to be distinguished, only a slight constriction of the light band is to be perceived at 35.

2 20 31.036 0.421 between 42 and 43
0.443 „ 36 and 37
0.450 „ 34 and 35
0.466 „ 32 and 33

2 50 31.22 the outer bath is further kept at this temperature

2 50 31.050 the rise of the temperature of the inner bath is now exceedingly regular

4 30 31.096 0.443 in the middle of 53
0.450 between 32 and 33
0.466 „ 24 and 25

The mist in the tube is now equally dense everywhere, and becomes gradually less, the moving apart of the three still descending bulbs continues slowly and regularly

8 7 31.210 0.466 lies just on the bottom
0.450 between 36 and 37; has risen 4 mm in $2^h15'$ and so shows a tendency to move to the top.

8 10 The cooling takes place by reducing the outer bath to a lower temperature

8 30 31.133 0.466 begins to rise from the bottom
0.450 at the same place

8 35 Throughout the tube a bluish mist appears

8 40 This mist gets denser

8 50 At [15] a thick milky white mist is formed, which spreads rapidly upwards and downwards.

30.984 At [10] the meniscus appears. From the upper place of contact of the thermo-elements drops fall down, from the lower place of contact smaller gas bubbles rise upwards. (The cooling proceeds too rapidly). The meniscus rises, 3 bulbs fall quickly into it from above, and 1 rises towards it from the bottom.

The differences of temperature within the tube were found to be between $0°.02$ and $0°.03$, but in consequence of disturbances they were often not to be observed. In the observation of 8^h7 they were no more than $0°.01$.

July 5 1906.

In the *second experiment* the heating took place somewhat more rapidly. In $1^h10'$ the inner bath was brought at

$9^h10'$ 29°.99 The separation of the bulbs has, of course, not advanced so far as in the first observation, and the deflections of the galvanometer were larger. The tube remained now farther behind the temperature of the waterbath.

9 40 31.60 [36] The meniscus is still dimly to be distinguished here, and a thin light mist is visible through the whole tube. Under the meniscus a somewhat darker band of a light brown colour is seen.

The position of the bulbs is now
0.365 at the top
0.390 between 43 and 44
0.405 „ 42 and 43
0.421 in the middle 41
0.443 „ „ „ 40
0.450 „ „ „ 39
0.466 between 37 and 38
0.483 and 0.510 on the bottom.

31.7 0.390 and 0.405 now go very rapidly to the top followed by 0.421.

At the place of the meniscus now only a slight constriction and a light brown mist band are to be perceived.

10 45 31.900 The temperature is then kept constant till 11^h37 with no greater deviation than 0°.004 and then from

11 37 31.888 till 2^h15 with no more deviation than 0°.002.

2 15 The mist has now entirely vanished and the bulbs are all apart.

0.510, 0.483, 0.466 on the bottom
0.450 and further ones in the top, none of the bulbs remain suspended in the body of the tube; the bulb 0.450 was the last to go to the top, whereas 0.466 had already been on the bottom for some time.

A difference of temperature is no longer to be perceived.

At first the cooling took place more slowly.

3 31.550 A slight mist is perceived

3 45 31.040 the mist has become distinctly denser.

5 10 30.985 [5]. In this position the meniscus originates in a milky cloud in the lower part of the tube. Further the lowering of the temperature proceeds too rapidly.

5 25 30.950 [14]. Three bulbs float in the meniscus. A disturbance in the regulation of the temperature of the outer bath put a stop to the experiment.

July 11th 1906.

A *third experiment* did not give any difference with the first with slow heating. The temperature was kept still closer to the critical, and the heating went still more slowly. Now the meniscus descended, and the brown colour under the meniscus was particularly pronounced, it was darkest just below the meniscus, and gradually faded downward. After a slow heating which extended over $10^1/_2$ hours the meniscus disappeared at

6h 30°.986. The position of the bulbs was now

0.443 between 34 and 35
0.450 in the middle 27
0.466 between 25 and 26.

In consequence of a slight disturbance in the regulation of the outer bath t_i descended to

6 45 30.984 [25] the meniscus appears, the position of the highest bulb does not undergo any change, the two others 0.450 and 0.466 float in the meniscus.

9 15 31.010 the meniscus disappeared somewhat lower, the brown colour in the lower half is much more intense, at last it contracted to a dark brown band of ± 1 mM. width just below the meniscus. Gradually it grew lighter and shortly after the meniscus it also disappeared ;

0.443 between 41 and 42
0.450 . . . . . 23 and 24
0.466 in the middle 22.

The temperature at the top of the tube was 0°.01 higher than at the bottom.

§ 8. *Conclusions and remarks.* An elaborate discussion of the observations in connection with other peculiarities of the net of isotherms in the neighbourhood of the critical state (cf. Comm. n°. 74 and Comm. n°. 88 IV § 5, Jan. 1904 and Comm. Suppl. n°. 10), and as to those on the mist in connection with the observations of Gouy,

TRAVERS and USHER and YOUNG [1]), must be deferred to a later occasion. However, some conclusions are obvious.

As the temperature rises more slowly and the equilibrium in the tube is better reached, we can get nearer to equality of density of the vapour and liquid phases. We think we found a smaller difference in density in our measurements than any of the observers before us [2]).

We did so in the third experiment. The critical temperature was then fixed between 30°.984 and 30°.986 [3]). That at 30°.984 only a small difference in density existed between liquid and vapour appears as follows: When the meniscus appeared we found 0.443 for the density of the vapour at the height 35. So we estimate the density at 0.452 at the height of the meniscus (25) according to the correction of § 5 (doubtful); bulb 0.450, however, floats on the meniscus. The density on the bottom is < 0.483 (height (see § 7 beginning) 5 cm. under 30), so we estimate the density of the liquid at 0.468 at the height of the meniscus; bulb 0.466 floats. Vapour and liquid differ, therefore, certainly less than $^1/_{10}$, and probably no more than $^1/_{20}$ in density. In the first experiment we found $\varrho_v > 0.421$, $\varrho_l < 0.483$ from which $\varrho_v > 0.430$, $\varrho_l < 0.468$ follow with the estimated correction for gravity; so under these less favourable circumstances a difference of less than $^1/_{10}$ is most likely realized. These results concerning the closer and closer approach of the density of liquid and vapour, which quite agree with the views of ANDREWS-VAN DER WAALS, deprive the much larger differences of phases at the same temperature and pressure above the critical temperature, which TEICHNER derives from his experiments, of all importance [4]).

---

[1]) This includes the discussion of the mist stage of VON WESENDONCK, which would constitute the transition stage in the neighbourhood of the critical state, and which in any case can only extend over a small part of the region of density and temperature where a mist can be seen.

[2]) YOUNG, Journ. Chem. Soc. 71 (1897) p. 455 stated at 0°.05 below the critical temperature a difference of 14% between the liquid and vapour densities. [Note added in the translation].

[3]) The readings of the temperature have been reduced to those on a thermometer which had been controlled with an air thermometer accurate up to 0°,01 by the Phys. Tech. Reichsanstalt. Our result agrees with that of KEESOM, 30°.98 (Comm. N°. 88 see above), made with the same thermometer. Moreover, besides and after the determinations of the critical temperature of CO_2 cited in LANDOLT-BÖRNSTEIN-MEYERHOFFER'S Phys. Chem. Tables are to be mentioned: VERSCHAFFELT Zitt. Versl. Juni '96 (31°.0), VON WESENDONCK Verh. d. Deutsch. Phys. Ges. 5 p. 238 (30°.95), BRINKMAN Diss. Amsterdam 1904 (31°.12).

[4]) It is true we might assume that the equilibrium of liquid and vapour with so slight a difference of density as we observed, is only reached after so long a time as was allowed in this experiment to obtain equilibrium of temperature and that at first states with greater difference of density of liquid and vapour (cf. note 1 p. 1 § 1) appear at the same temperature, which gradually pass into the final

It is in harmony with this that a tolerably sharply defined critical density can be assigned. We derive 0.460 from the density of vapour and liquid in the third experiment for it, which agrees with the mean which would follow from experiment 1 at 2^h15, i.e. 0.450, and 0.470, derived from experiment 3 on account of the appearance of the meniscus at 25 (cf. further § 6 p. 223 footnote 1).

Differences of density as TEICHNER finds, were also found by us; it was in the second experiment at the moment that the meniscus disappears with comparatively rapidly rising temperature. However, after the tube has been kept at the same temperature above the critical temperature for 3 hours, and the temperature in the tube has become uniform probably up to less than 0°,01 0°,9 above the critical temperature, they have been reduced to less than 0,466 — 0,450, or less than 3,5 %, i. e. after correction for gravity $< 3{,}3$ % over 10 cm.

The remaining difference in the first experiment 0°,23 above the critical temperature after 6 hours' heating above the critical temperature can be derived from the fact that bulb 0.450 floats 5.6 cm. above 0,466. This difference is no more than 3,5 %, and corrected for gravity 2,9 %.

From VERSCHAFFELT's calculations follows that at 0°,23 above the critical temperature 0,0001 molecule of admixture may cause about 12 % difference of density. Differences of temperature and admixtures which may account for remaining differences such as those just treated are scarcely to be avoided even with the precautions taken by us.

Nothing has been observed of an "Entmischung" by cooling when the critical temperature is approached, as TRAUBE l.c. p. 477 mentions.

TEICHNER observed that, after the disappearance of the meniscus, at the place where it was found last a transition zone exists towards which the differences of density concentrate, whereas outside it the changes are only insignificant. In our observations the contrary appeared, and the changes in density continue regularly with increase of temperature, only the motion of the bulbs was slightly accelerated as they approach the top of the tube, and they cover the last 1 or 2 cm. very rapidly. In a less degree but in the same way this takes place with the bulbs which descended. We consider these phenomena to be connected with heating and cooling of phases by compression and expansion [1]).

state with simultaneous change of the pressure of coexistence (cf. note 1 p. 1 § 1). But the absence of subsequent rise of pressure in the repetition of DE HEEN's experiment (see § 3) has taught us, that already after a very short time after-changes of the density no longer occur.

[1]) They just as the "Entmischung" assign that the temperature differences within the tube in the experiments of TEICHNER were probably greater than in ours. [Note added in the English translation].

Physics. — "*Contributions to the knowledge of the ψ-surface of* VAN DER WAALS. XV. *The case that one component is a gas without cohesion with molecules which have extension. Limited miscibility of two gases.*" (Continuation). By Prof. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. Supplement N°. 15 to the Communications from the Physical Laboratory at Leiden.

(Communicated in the meeting of May 24, 1907).

§ 8. *On the temperatures and the pressures on the gas-gasplait.* In order to form a provisional opinion as to the experimental conditions which must be satisfied that limited miscibility in the gas state may be observed, and to be able to derive what pairs of substances must be considered suitable for this purpose, it is desirable to examine for some cases what temperatures and pressures occur on the gas-gasplait [1]). In the case (§ 2, March '07) of a component without cohesion [2]) or almost without cohesion ($m < m_1$, see § 7), the gas-gasplait will occur for all temperatures between the critical temperature of the less volatile component and the critical temperature of complete miscibility [3]). Its pressures will then be larger than

[1]) In our opinion Mr. VAN LAAR (These Proc. May '07, p. 35, note 2) is wrong in thinking that in the case of a three-phase-equilibrium, as e.g. in the system water-ether, our terminology with regard to the distinction between gas and liquid does not agree with that used by VAN DER WAALS. According to what has been said about this distinction in § 4, for a three phase equilibrium of a system of the type water-ether the denser phase which is rich in water, *must* be called liquid as belonging to the liquid branch of the connode, just as the less dense phase which is rich in ether, *must* be called gas phase; whether the denser phase which is rich in ether is to be called liquid or gas, is not determined by the principle of the continuity of the phase along the connode; if the reduced temperatures at which this phase appears, are taken into account, also the last mentioned phase will be called liquid for the system ether-water in accordance with what has been said in § 4.

[2]) The second branch of the plaitpoint curve in Fig. 1 § 2 (These Proc. March '07, p. 787), about which VAN LAAR speaks in These Proc. May '07, p. 36, has there ($a_{22} = 0$) contracted to a point $x = 1$, $v = b_{22}$. It is true that in the case of our § 7 (Plate II, These Proc. March '07) a second branch of the plaitpoint curve occurs, but it has been explicitly stated there (p. 795 at the bottom and p. 797) that we did not discuss the spinodal curves at the lower temperatures at which this branch of the plaitpoint curve makes its influence felt, referring inter alia with a view to these temperatures to VAN LAAR's papers.

[3]) As mentioned in § 1 this idea was introduced by VAN DER WAALS, who also gave the formulae for the calculation of this temperature (VAN LAAR calls it "third critical temperature").

the critical pressure of the least volatile component. If the suppositions mentioned in § 2 might be applied for this, and the values of a_M and b_M for He might be borrowed from Comm. N°. 96^c, Febr. '07, p. 660 footnote 2, so that $a_{MHe} = {}^1/_{175}\, a_{MH_2} = 0.0000024$ and $b_{MHe} = {}^1/_3\, b_{MH_2} = 0.00044$, this case would be realized for mixtures of He and water [1]). Then we should find $T_{km} = 1.056\, T_{k_1}$, so that the gas-gasplait would occur over a range of temperature of 36° above 365° C., and at pressures above 195 à 200 atms.

In the case that the molecules of the least volatile component act on each other feebly, but still exert such an attraction that a double plaitpoint [2]) occurs in the net of the spinodal curves, the pressure in this plaitpoint and its temperature in connection with the critical temperature of complete miscibility give important indications as to the pressures and temperatures of the gas-gasplait.

In table II these data, calculated for the case that the suppositions

TABLE II.

Pair of substances	T_{km}/T_{k_1}	T_{dpl}/T_{k_1}	T_{dpl}/T_{kx}	p_{dpl}/p_{k_1}
Hydrogen-helium	0.933	0.915	4.44	41.6
Oxygen-helium	0.962	0.957	8.64	61.3
Argon-helium	0.970	0.962	7.90	64.5
Neon-helium	1.007	0.961	3.72	18.8
NO-helium	1.031	0.991	3.76	13.1
NH_3-helium	1.009	0.969	6.20	25.2
H_2S-helium	0.972	0.970	13.79	171
CO_2-helium	0.9540	0.9536	15.89	1045

[1]) The a_M and b_M for water have been borrowed from LANDOLT-BÖRNSTEIN-MEYERHOFFER's Physik. Chem. Tabellen.

[2]) The appearance of a double plaitpoint near K_m was already observed by VAN LAAR (These Proc. May 1905 p. 42). The conditions for its appearance, however, were not correctly defined by him (cf. § 9 II). In view of this latter fact we thought that we drew sufficient attention to this result of VAN LAAR by referring the reader to VAN LAAR's papers. (see p. 797 footnote 1). The detaching of a longitudinal plait at high temperatures, which leaves the ψ-surface with its open side turned to $v = b$, follows immediately (see These Proc. April '07 p. 848 footnote) from the general considerations and calculations of VAN DER WAALS Cont. II § 19 sqq. and VAN DER WAALS' diagram in Zittingsverslag Kon. Akad. Nov. 1894 p. 133, when the case *a*) cf. § 9. I, a case which VAN LAAR has not included in his considerations, does not occur.

mentioned in § 2 might be applied, have been given for some helium mixtures. T_{km} has here been calculated according to VAN DER WAALS Cont. II, p. 43 (cf. § 6), T_{dpl} according to the formula mentioned in § 7, p_{dpl} from the equation of state with the just mentioned T_{dpl} and the v_{dpl} also represented in formula in § 7 [1]).

The reduced temperature of the double plaitpoint T_{dpl}/T_{kx}, mentioned in this table, gives an idea in how far the phases in its neighbourhood behave as compressed gas-phases.

The values of a and b of the different components have been borrowed from KOHNSTAMM, LANDOLT-BÖRNSTEIN-MEYERHOFFER's Physik. Chem. Tabellen; for those of helium see above; for neon we have made use of the ratio of its refractive power [2]) to that of helium according to the determinations of RAMSAY and TRAVERS [3]), and of the estimation concerning the critical temperature by TRAVERS, SENTER and JAQUEROD [4]).

It appears from table II that when the gas-gasplait can make its appearance, the range of temperature within which this is the case (between T_{km} and T_{dpl}), on the mentioned suppositions is small for most of these pairs of substances, for some even exceedingly narrow.

For the pressures on the gasplait higher values than p_{dpl} will have

---

[1]) Though originally we did not consider the developments which led us to the explicit expressions for the double plaitpoint mentioned These Proc. March '07 pp. 796 and 798 of sufficient importance, now that VAN LAAR (see These Proc. May '07 p. 41) thinks the derivation of such like expressions impossible there is a reason for communicating them on a following occasion.

[2]) HAPPEL, Habilitationsschrift Tübingen 1906, p. 30, found that the refractive power for argon, crypton and xenon would yield values for b which greatly deviate from the b's derived from the critical data. When according to the principle of the corresponding states (cf. HAPPEL loc. cit. p. 31, note 1) we compare the ratios of the refractive powers for these gases with those of their critical volumes (derived from p_k and T_k) the deviations are far less considerable. So with regard to this property, these one-atomic gases form a group, just as is the case with the bi-atomic and with a great many more-atomic substances (GUYE, Journ. de phys. (2) 9 (1890) p. 312).

[3]) RAMSAY and TRAVERS, Phil. Trans. A197 (1900) p. 81. Yet we must remark that when comparing this ratio for helium and argon according to RAMSAY and TRAVERS with the ratio of b_{He} according to our estimation and b_A derived from p_k and T_k, we should find an important deviation (cf. note 1). Also in view of this the data concerning mixtures of helium and neon are very uncertain.

[4]) TRAVERS, SENTER and JAQUEROD, Phil. Trans. A 200 (1902) p. 177. Their views, however, on a connection between atomic weight and critical temperature lead to an unlikely result for the critical temperature of helium.

The determinations of isotherms of neon by RAMSAY and TRAVERS, loc. cit. have been of as little use to us as those of helium for the determination of a and b (different particulars in the course of the isotherms of the one-atomic gases given by these scientists in plate 2 loc. cit. do not seem very probable to us).

to be expected as a rule. Thus it appears from table II that these pressures become very high, if the circumstances are not very favourable.

It would have a very favourable influence on the circumstances of temperature and pressure at which limited miscibility in the gas state might be observed, if it should prove that for mixtures of helium with another gas a_{12M} is smaller than is expressed by $\sqrt{a_{11M}\, a_{22M}}$ [1]).

§ 9. *Mr.* VAN LAAR's *remarks*, (These Proc. May '07 p. 34—46) which imply that we have set forth some of our results as new, whereas they had been already derived and published by him before, compel us to the following explanations in order to show the incorrectness of these assertions.

I. As to part of these observations, they are best refuted by shortly repeating the train of thought followed by us.

When we applied the equations laid down by VAN DER WAALS with regard to the spinodal curve [2]) in Cont. II, § 19 sqq., transferred to the ψ-surface for the unity of weight, to the case that one of the components is a gas without cohesion [3]) with molecules which have extension, we arrived on the suppositions [4]) mentioned in § 2 at a *plait which starts from the side of the small volumes, comes*

---

[1]) These Proc. March '07 p. 796 note 1, and VAN DER WAALS These Proc. April '07 p. 831.

[2]) The equation for the spinodal curve of the molecular $\downarrow$-surface (cf. VAN LAAR These Proc. May '07 p. 37 at the top) was given by VAN DER WAALS in Cont. II. p. 45, equation (1) in a form which after substitution of $\frac{da}{dx}$, $\frac{db}{dx}$ and $\frac{d^2a}{dx^2}$ passes immediately into that used by VAN LAAR. (See VAN LAAR, These Proc. May '05 p. 33 at the bottom). The equation given by us p. 788 referred to and was derived from the equation for the $\downarrow$-surface for the unity of weight (These Proc. Dec. '06 p. 510). For the rest we differ from the opinion repeatedly expressed by VAN LAAR (inter alia These Proc. May '05 p. 34), that it would be more difficult and more elaborate to derive the equation of the spinodal curve and also that of the plaitpoint curve from the ψ-function than to do the same from the ζ-function.

[3]) This investigation was announced in Comm. No. 96*b*, Dec. '06 p. 502.

[4]) When we were not allowed to put $\frac{\partial^2 b}{\partial x^2} = 0$ for and in the immediate neighbourhood of $v = b$, as we did (cf. VAN DER WAALS Cont. II p. 42), the spinodal curve will always be closed towards the side $v = b$ as VAN DER WAALS observes l.c. and These Proc. April '07 p. 848. It is then to be expected, at least for small $\frac{\partial^2 b}{\partial x^2}$, that the plait in question makes its appearance for the first time at a maximum plaitpoint temperature, and for the rest extends to the large v's in the same way as the plait described here.

into contact with the line $x = 0$ *at a certain temperature, and crosses in a slanting direction from* $v = b$ *to the side* $x = 0$ *at lower temperature* (§ 2 These Proc. March '07 p. 787). Comparison of this result with VAN LAAR's papers induced us then to cite (p. 786 footnote 1) that the latter already treated the projection of the plaitpoint curve on the v, x-plane for the case of a gas without cohesion, but without further investigating the shape of the spinodal curve and of the plait for this case. Now that VAN LAAR (These Proc. May '07 p. 35) says: "The case that a plait *starts from* C_0 [1]) *to* C_2 [2]), or also at the same time from C_2 to C_0 (when there is a minimum temperature in the plaitpoint line) is not new (see KAMERLINGH ONNES and KEESOM, p. 788 below), but has been before described and calculated by me in all particulars", we have once more looked through his papers.

It would have been good if Mr. VAN LAAR had indicated the place where we had to look for this description of the plait treated in § 2 and indicated by VAN LAAR in the italicized words (the italics are ours); we have not been able to find this description in his preceding papers even on this renewed careful perusal [3]).

That the shape of the plait described by us occurs for temperatures above the critical temperature of the least volatile component led us to the considerations on limited miscibility in the gas state mentioned in § 3 sqq.

Always availing ourselves of the above mentioned equations of VAN DER WAALS, we examined then if also with $a_{22} > 0$ such a plait may occur for values as they are to be expected for mixtures with helium. We saw in § 7 (These Proc. March '07 p. 795) that for the case of the plaitpoint curve running from K_1 to K_m (called type I by VAN LAAR) 3 cases are to be distinguished: *a*) that with falling temperature the plaitpoint gets from K_m on the ψ-surface, and proceeds regularly towards K_1; *b*) that with falling temperature a plaitpoint coming from K_m and one coming from K_1 unite to a double plaitpoint; *c*) that the plaitpoint gets from K_1 on the ψ-surface and proceeds regularly towards K_m (without double plaitpoint with minimum

---

[1]) Our K_m.

[2]) Our K_1.

[3]) On the contrary he says in his paper These Proc. Sept. 1906 p. 231 (cf. VAN LAAR, These Proc. May 1905, p. 42 at the bottom): ": In former papers it has been demonstrated that in the neighbourhood of C_0 a minimum plaitpoint temperature makes its appearance both with type I in the line C_0C_2 and with type II in the line C_0A, and that therefore with decrease of temperature a *separate plait* begins to detach itself starting from C_0 at a definite temperature T_0 (the plaitpoint temperature in C_0), which plait will merge into the main plait (or its branch plait) later on in an homogeneous double point.

plaitpoint temperature). The conditions for the occurrence of these cases were defined by us by means of the equations (2) and (3) there. From this appeared that with very feeble attraction the case *a*) occurs, with greater attraction the case *b*), whereas with still greater attraction case *c*) occurs (supposing the system to belong to type I).

We have found neither the case *a*) as we already observed above, nor the case *c*) in VAN LAAR. We did find the case *b*), chiefly with regard to the treatment of what takes place at lower temperatures, when three-phase-equilibria occur. For this treatment we referred to VAN LAAR (cf. These Proc. March '07 p. 797).

From the fact that VAN LAAR has declared this shape *b*) to hold universally for type I (cf. p. 235 footnote 3; see also VAN LAAR p. 36) it appears in our opinion, that VAN LAAR has not only left the cases *a*) and *c*) unmentioned, but has decidedly overlooked them. [1])

II. One more remark remains to be discussed. In § 7 we put as the *two* criteria of the case *b*), the course of the plaitpoint curve being from K_1 to K_m (see above), in which case a minimum plaitpoint temperature occurs (supposing $b_{22M} < b_{11M}$):

$$\sqrt[4]{a_{22M}/a_{11M}} > \frac{1}{3}\left\{-1 + \sqrt{1 + 3\,b_{22M}/b_{11M}}\right\}$$

and

$$\sqrt[4]{a_{22M}/a_{11M}} < -(1 - b_{22M}/b_{11M}) + \sqrt{1 - b_{22M}/b_{11M} + (b_{22M}/b_{11M})^2}.$$

Mr. VAN LAAR points out (These Proc. May '07, p. 45, appendix), that the first-mentioned condition corresponds with a condition for the occurrence of a minimum plaitpoint temperature, derived by him These Proc. Dec. '05, p. 581 (and VERSCHAFFELT These Proc. March. '06 p. 751). In our opinion, however, Mr. VAN LAAR is mistaken when he thinks that the *one* condition stated by him is sufficient in all cases to decide as to the occurrence of a minimum plaitpoint tem-

[1]) We might consider the course of the spinodal curves in case *b*), if this is also extended to values of $x > 1$ and < 0, and of $v < b$, as a more general case, from which the cases *a*) and *c*) might be obtained, at least qualitatively and when we restrict ourselves to the region of the ψ-surface ($1 > x > 0$ and $v < b$) that is of importance for the treatment of mixtures. This might be done by cutting out a region bounded by $x = 0$ and $x = 1$, and a suitable line $v = b$ in the same way as VAN DER WAALS These Proc. Feb. '07, p. 621 sqq. treats the course of the isobars (cf. § 7 p. 796 of this Communication). We have not found a single indication that VAN LAAR's description of case *b*) is to be interpreted in this way; from the phrase, quoted p. 235 footnote 3 e.g. we should much sooner conclude to the contrary.

At any rate the distinctions which are of physical importance, have not been made.

perature. Nor can his considerations of Dec. 1905 give an indication to conclude to the occurrence of a minimum plaitpoint temperature in the branch $K_1 K_m$ of the plaitpoint curve. For there VAN LAAR starts from the value of $dT_{xpl}\ dx$ at the critical temperature of the most volatile component called T_{k_2} by us. The condition that at T_{k_2}, the *lower* of the critical temperatures of the components, $dT_{xpl}/dx < 0$, implies that *if the plaitpoint curve crosses from* K_2 *to* K_1, a minimum temperature must occur in it.[1]) VAN LAAR (These Proc. May '07 p. 43), considers now the value of dT_{xpl}/dx for the least volatile component (for K_1). It is clear in our opinion, that at the *highest* critical temperature the condition $dT_{xpl}/dx < 0$, which coincides with the first of the inequalities mentioned (cf. p. 797 last sentence of the alinea at the top), does not give any indication to conclude to the occurrence of a minimum plaitpoint temperature. That if for K_1 $dT_{xpl}/dx < 0$, really *one* of the conditions for the occurrence of a minimum plaitpoint temperature in the branch $K_1 K_m$ of the plaitpoint curve has been fulfilled, VAN LAAR has, in our opinion, only shown by his considerations on the situation of the double plaitpoint. not given until April (translated in These Proc. of May) at the same time with his remarks, which considerations agree with those which had led us a month before to the statement of the two conditions mentioned.

---

[1]) Only if the plaitpoint curve crosses from K_1 to K_2, this condition is sufficient to conclude to the occurrence of the minimum plaitpoint temperature (cf. VAN LAAR p. 46); for if the branch of the plaitpoint curve starting from K_2 bends round to VAN LAAR's point A ($x = 1$, $v = b_{22}$ in our notation), we cannot speak of a minimum plaitpoint temperature in the sense which is generally attached to this word.

A similar consideration gave rise to our remark in note 2 p. 795, which remark we are obliged to maintain in spite of Mr. VAN LAAR's contradiction, p 46. (Wrongly Mr. VAN LAAR thinks there, note 1, that in our note instead of "maximum-temp." "minimum-temp." should be read, which might also immediately appear by comparison with the cited text of VERSCHAFFELT).

Physics. — *"Some remarks on the last observations of Prof.* H. KAMERLINGH ONNES *and Dr.* W. H. KEESOM." By Mr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

In the Proceedings of May 24 (1907) Prof. KAMERLINGH ONNES and Dr. KEESOM answered some remarks which I published in the Proceedings of April 26 (1907) (in reference to their last papers).

I may be allowed to revert briefly to the chief points of this answer.

a. P. 235, line 14—18: "It would have been good", etc.

In fact the course of the *plait* in the case referred to by Prof. KAMERLINGH ONNES and Dr. KEESOM has not been given by me. I confined myself to investigating the course of the *plaitpoint line* in general. The results which I obtained on this point harmonize fully with what was found by KAMERLINGH ONNES and KEESOM.[1])

b. P. 236, line 7—15.

In my papers published in These Proceedings only the case *b* has been mentioned (in which a minimum temperature occurs on the branch C_0C_2 of the plaitpoint line). The reason of this is, that I then (7 June 1905 and 10 January 1906) only worked out the case $b_1 = b_2$, in which such a minimum always occurs.[2]) The formulae which I developed afterwards for the general case $b_1 \lessgtr b_2$ (see TEYLER I, II and III), [which last publication (viz. III) was delayed by circumstances independent of my will], contained the *possibility* of the three cases *a*, *b* and *c*. As a matter of course Prof. KAMERLINGH ONNES and Dr. KEESOM could not take this yet unpublished investigation into account, and I only mention the fact to prove that the *possibility* of the cases *a* and *c* had not escaped my notice.

c. P. 236. "In our opinion, however, Mr. VAN LAAR is mistaken when he thinks that the one condition stated by him is sufficient in all cases to decide as to the occurrence of a minimum plaitpoint temperature."

---

[1]) At the same time I am glad to declare that I completely acknowledge the priority of Prof. KAMERLINGH ONNES and Dr. KEESOM in bringing to light the possibility of plaits which proceed without minimum from C_1 to C_2 and inversely (cases *a*. and *c*. of KAMERLINGH ONNES and KEESOM), the knowledge of which is necessary for understanding the behaviour of binary mixtures, containing as one component a substance with weak attraction.

(Note added in the English translation).

[2]) Afterwards I have seen that also for $b_1 = b_2$ the case *a*. does occur, when it is not supposed that $T_0 < T_2$. (Note added in the English translation).

I may remark about this that I have meant nothing else — which it seems, I ought to have set forth more clearly — but to conclude to the existence of the minimum temperature, when the plaitpoint temperature at the extremity of the branch of the plaitpoint line where the condition in question is fulfilled, is *lower* than at the other end of that branch, in which case this one condition is really sufficient.[1])

ERRATA.

In the Proceedings of the meeting of February 1907:

p. 660 l. 5 from the bottom: for "least" read: "most"
p. 662 table II in the heading read $M_2/M_1 = 2$

In the Proceedings of the meeting of March 1907;

p. 765 l. 13 from the top: read:

$$\left[\frac{(pv_A)_{t''} - (pv_A)_{t'}}{t'' - t'}\right]_{v_A} = \left(\frac{\overline{dpv_A}}{dt}\right)_{t'}^{t''}$$

table VII, for: a_p read: $\frac{\overline{dpv_A}}{dt}$

p. 778 l. 13 and 14 from the top: for a_p read: a_v
p. 785 l. 17 from the bottom: Insert:
For the temperatures in liquid hydrogen first the correction is to be applied which will prove to be necessary according to Comm. N°. 95ᵉ § 3*b* and § 8.

p. 796 the value for $\frac{x_M}{1-x_M}$ given in equation (1) is to be multiplied by $\sqrt{a_{11M}/a_{22M}}$.

---

[1]) But I readily concede that Prof. KAMERLINGH ONNES and Dr. KEESOM have been the first to deduce both conditions for the minimum and to take in consideration the cases *a* and *c*. (Note added in the English translation).

(October 31, 1907).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday October 26, 1907.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 26 October 1907, Dl. XVI).

CONTENTS.

H. ZWAARDEMAKER: "About odour-affinities", p. 242.

H. J. HAMBURGER: "A method to extract enzymes and pro-enzymes from the mucous membrane of the digestive tube and to establish the topic distribution of them", p. 250.

J. A. BARRAU: "The extension of the configuration of KUMMER to spaces of (2^p-1) dimensions". (Communicated by Prof. D. J. KORTEWEG), p. 263. (With one plate).

LUCIEN GODEAUX: "The theorem of GRASSMANN in a space of n dimensions". (Communicated by Prof. P. H. SCHOUTE), p. 271.

H. KAMERLINGH ONNES and W. H. KEESOM: "Contributions to the knowledge of the ψ-surface of VAN DER WAALS. XVI. On the gas phase sinking in the liquid phase for binary mixtures in the case that the molecules of one component exert only a feeble attraction", p. 274. (With one plate).

C. A. PEKELHARING: "An investigation of Mr. J. W. A. GEWIN, on the relation of pepsin to chymosin", p. 283.

P. ZEEMAN: "The intensities of the components of spectral lines divided by magnetism", p. 289. (With one plate).

P. VAN ROMBURGH: "On lupeol", p. 292.

E. VAN EVERDINGEN Jr.: "Relations between mortality of infants and high temperatures". (Communicated by Prof. C. H. WIND), p. 296.

R. A. WEERMAN: "Action of potassium hypochlorite on cinnamide", (2nd communication), (Communicated by Prof. S. HOOGEWERFF), p. 308.

J. P. VAN DER STOK: "The analysis of frequency-curves of the air-temperature", p. 309.

L. BOLK: "Is red hair a nuance or a variety?", p. 321.

Erratum, p. 329.

Physiology. — *"About Odour-affinities"*. By Prof. H. ZWAARDEMAKER.

(Communicated in the meeting of September 28, 1907).

The great number of odours occurring in nature and in technics may, by virtue of the current opinions in literature, be divided into 9 classes, which may be indicated by historical names [1]), chiefly borrowed from Linnaeus. These classes are: etherial odours, aromatic odours, odores fragrantes, moschus odours, allyl odours, empyreumatic odours, capryl odours, narcotic odours, odores nauseosi. I have selected from each class a representative which, chemically well characterized, can in a very simple way be made fit for olfactometric investigation (by dissolving the chemically pure odoriferous material in paraffinum liquidum [2]), with one exception, viz. muscon, which is odourless in by itself odourless paraffine, and which therefore has been used mixed with myristine acid. They are:

isoamylacetate	0.5%
nitrobenzol	5%
terpineol	2.5%
muscon	0.627%
aethylbisulfide	1‰
guajacol	1‰
valerian acid	1‰
pyridine	1%
scatol	1‰.

If in the double olfactometer two of these materials are joined together, there occur among the 36 combinations thus obtained no real mixed odours, but because they are counterbalancing each other, either an odourless mixture or rivalry is obtained. Odourlessness, respectively indefiniteness of odour, with change into odourlessness by rarefaction of the airmixture, is met with, when the stimuli are weak; rivalry, i. e. the alternate preponderance of one or the other of the two mixed odours is met with, when the stimuli are strong. However, also in the last case the impression, made by the mixture, is considerably weaker than the impression that every odour by itself brings about.

As unit of smelling-power I take the olfaction, i. e. the smallest quantity of odour of a definite quality, which can be recognized

[1]) H. ZWAARDEMAKER, Physiologie des Geruchs. Leipzig 1895 p. 207.

[2]) Not water, but paraffinum liquidum has been chosen as a solvent because it is desirable to work for months at a stretch with the same cylinders without alteration of the solution.

by a normal organ of smelling ("Erkennungsschwelle", "recognizing-limit").

If the above mentioned paraffinic solutions are evaporated at a temperature of 15° C. and give off smelling material to a current of air brushing past with a velocity of 75 cub. cm. per sec., one olfaction will be communicated to the latter per 50 à 100 cub. cm. of air by shoving out the cylindric evaporating surface to a definite cylinderlength. This cylinderlength amounted on an average:

for the		isoamylacetate-solution	to 0.2	cm.
„	„	nitrobenzol-solution	„ 0.03	„
„	„	terpineol-solution	„ 1.1	„
„	„	muscon-mixture	„ 0.15	„
„	„	aethylbisulfide-solution	„ 0.015	„
„	„	guajacol-solution	„ 0.3	„
„	„	valerian acid-solution	„ 0.03	„
„	„	pyridine-solution	„ 0.02	„
„	„	scatol-solution	„ 0.003	„

In judging of this table, it should be taken into consideration that the numbers have sometimes been obtained by taking the cylinder-lengths during the experiment actually 10 or 12 times longer and by rarefying the air in the reservoir that is smelled at, 10 or 100 times. Thus the objection was obviated, on the one hand that small cylinderlengths should not be capable of being read with precision, on the other hand that the evaporation should not regularly take place from very narrow strips.

The mixing of the odours, which are to be joined together two by two, took place in a common reservoir, which, provided with two stop-cocks had been placed downstream the double olfactometer. The symmetry of the latter, in view of the resistance offered to the current of air, was previously examined by means of a bridge of Wheatstone applied to air-streams, while the purification of odours adhering by absorption between each number of two experiments has taken place by a permanent stream of air and electric warming of the wall of the reservoir. The reservoir in which the mixture takes place was smelled at by means of a separate tube, the down-stream cock being opened.

The 36 combinations procured indefiniteness of odour or rivalry, if p olfactions of one odour and 9 olfactions of the other showed a proportion of p/q, of the following amount:

TABLE.

Mixture	p q [1]	Degree of completeness of the compensation [2]
isoamylacetate and nitrobenzol	0 44	indefiniteness*
" " terpineol	1.32	moderately acid additional odour
" " muscon	0.0625	indefiniteness
" " aethylbisulfide	0.244	complete compensation*
" " guajacol	3	indefiniteness
" " valerian acid	0.01	rivalry
" " pyridine	3.6	indefiniteness*
" " scatol	0.0037	indefiniteness
nitrobenzol " terpineol	1.375	indefiniteness*
" " muscon	0.434	"
" " aethylbisulfide	0.111	"
" " guajacol	0.65	"
" " valerian acid	0.03	"
" " pyridine	3.	"
" " scatol	0.012	indefiniteness*
terpineol " muscon	0.125	"
" " aethylbisulfide	0.067	somewhat aromatic remainder
" " guajacol	1.	rivalry
" " valerian acid	0.05	almost complete compensation
" " pyridine	0.53	" " "
" " scatol	0.12	" " "
muscon " aethylbisulfide	1	indefiniteness
" " guajacol	0.03	tolerably satisfactory
" " valerian acid	2.7	almost complete compensation
" " pyridine	1.2	rivalry
" " scatol	0.2	indefiniteness*
aethylbisulfide " guajacol	0.056	rivalry*
" " valerian acid	1.2	indefiniteness
" " pyridine	3 2	very indefinite empyreum. odour
" " scatol	0.0075	indefiniteness
guajacol " valerian acid	0.03	"
" " pyridine	0.016	indefiteness*
" " scatol	0.0007	"
valerian acid " pyridine	4	"
" " scatol	1.2	"
pyridine " scatol	0.42	indefiniteness

The details of these experiments and more particularly the absolute quantities which were made to be the foundation of each combination of odours, will soon be communicated elsewhere in a more extensive treatise.

The proportional number given in the table holds good, besides for a definite average combination, also for an adjacent group of stronger, respectively weaker stimuli. For this zone holds good the rule that if p olfactions of an odour are compensated by q olfactions of another odour, this must likewise be the case for np and nq olfactions. FECHNER called the intensities of stimulus and sensation,

[1] $p < q$.

[2] Marked with an asterisk are those cases in which by an intentional experiment it has been proved that the proportional number is applicable to a certain zone of stimuli.

mutually increasing and decreasing in due proportion, the cardinal values of stimulus and sensation. By analogy we might speak here of cardinal values of the stimuli counterbalancing each other, leaving altogether out of the question whether this proportion will prove as easily explainable as that which FECHNER has in view. The zone for which the proportional number of the table holds good, may therefore be called the zone of cardinal proportions.

From the fact that at a simultaneous impression two odours can neutralize each other, it follows that the action of these stimuli on the organ may be represented by two vectors, standing as it were for two forces, which in general act more or less in opposite directions, the direction of the vector of the strongest odour (answering to q in the table) being chosen in such a way that the co-sine of the angle that it forms with the continuation of the vector of the weakest odour (answering to p in the table) is exactly equal to the proportion found for p/q in the combination concerned. For in this case the vector of the strongest odour may be thought to be replaced by the sum of two other vectors: one in a direction opposite to the vector of the weakest odour, and one at right angles to it (in the plane of the original vectors). If, moreover, the two original vectors are given equal length, each with such a unit of length as the proportional number implies, i. e. for the vector q and its components of q/p times more weight than for the vector p, the neutralization of actions that has to be symbolized by the original vectors, will have been accurately expressed. For the vector p and one of the components of vector q will represent equal, but opposite forces. We shall ouly have to consider the direction of the other component of vector q as direction of odourlessness, in order to have duly accounted for the complete lack of sensation.

A second set of vectors can be placed in the same system, provided the two sets have one vector in common. Starting from of a new proportional number p'/q' the new third odourvector that has been introduced, may then be given a definite direction with regard to the first odourvector; also the second and third vectors may be given their relative directions by means of a third proportional number p''/q''. The latter, it is true, can be done in two ways, according as the third vector is reached by a right- or a left-handed rotation starting from the vector answering to p, but of these two one may be chosen. To the combination p'/q' belongs a vector of odourlessness at right angles to the vector of weakest odour and to the combination p''/q'' a vector of odourlessness at right angles to the vector of weakest odour. The units of length of these vectors will in general

never be the same and also differ according to the combination that one has in view. As, however, we have never mutually combined three, but always two odours at a time, it will never be necessary to occupy ourselves with the units of length of the three at the same time, nor does this change of units, depending on the case considered, raise any objection. Even in our further demonstration this does not give rise to any difficulty, as we are never going to mutually compare vectors but when they have the same direction with regard to an independent vector that is at the same time considered, in other words possess with respect to the latter about the same units of length[1]).

A third set of vectors can, speaking generally, not be placed in the same system, even though it has one vector in common with the two preceding systems, for the fourth vector will in general have to be given different directions, according as it is considered in connection with the first and second, with the first and third or with the second and third. But what is in general impossible, may in special cases prove quite practicable. Let us consider this.

If we number our nine standard-odours with the figures 1 to 9 and likewise the corresponding vectors, each time two of these vectors can be fixed and the rest arranged with regard to these two vectors, which are definite in their situation. The question we put just now, comes to this: Is the mutual relation between the odours perhaps so as to make some of these last seven vectors coincide? In consequence of mistakes in the experiment a complete coincidence will no doubt be out of the question, but let us consider whether it happens within a margin of error of at most 1 % of 2π difference of direction ($= 3.6°$). For this purpose we have first combined 1 and 2, considering all the others with regard to these two; then 1 and 3 are fixed, the rest arranged according to this, etc. till all combinations, 36, have occurred. In each of the combinations seven vectors were met with, whose situation with regard to the two vectors previously chosen had to be traced in order to see whether they coincided or not. For each set of two previously determined vectors this gives rise to 42 judgments, so that in all 1512 judgments have

---

[1]) The proportional numbers as they have been empirically composed and taken together in our table, form 252 possible constellations of three vectors. Among them there is only one which, also as to the units, is completely satisfactory for all three proportions at the same time. It is the constellation in which terpineol, scatol and valerian acid are combined. The length of the vectors measured by means of a joint unit of length amounts in this case to 1 for the terpineol-vector, 8 for the scatol-vector and 20 units for the valerian acid vector.

been necessary for 36 combinations. However, as each case is repeated once, there are in reality 756 separate judgments.

Just now we said it was necessary that never other vectors than those about equally directed, which accordingly possess about the same unit of length, should be mutually compared. If we keep this in view, the following constellations are identical within a limit of 1 %:

isoamylacetate and nitrobenzol valerian acid and scatol	each four times
isoamylacetate and guajacol nitrobenzol and guajacol muscon and scatol aethylbisulfide and valerian acid	each three times
isoamylacetate and terpineol isoamylacetate and aethylbisulfide nitrobenzol and terpineol terpineol and guajacol muscon and aethylbisulfide muscon and valerian acid aethylbisulfide and scatol	each once

together 27 constellations [1]).

Some of these 27 constellations give rise to reciprocity, in such a way, that the vectors which are identical to two previously determined vectors, make the latter identical, when they themselves are previously determined in their mutual situation. This occurs in:

isoamylacetate and terpineol	← with regard to	muscon and scatol	→ with regard to ←	isoamylacetate and guajacol

Though the coincidence of two odour-vectors, if considered with respect to two other odour-vectors, is already very remarkable, a coincidence of 3 vectors is still more interesting. This has been realized in the following cases, if we extend the limit of error to 2%:

---

[1]) This figure rises to 42, if besides complete coincidences also coincidences with reciprocal values are taken into consideration.

isoamylacetaat, terpineol, guajacol } with regard to muscon and scatol

nitrobenzol, terpineol, guajacol } with regard to aethylbisulfide and scatol

muscon, valerian acid, scatol } with regard to isoamylacetate and terpineol

aethylbisulfide, valerian acid, scatol } with regard to nitrobenzol and terpineol

Even a coincidence of 4 vectors, has been found once, and that for:

isoamylacetate, nitrobenzol, terpineol, guajacol } with regard to valerian acid and scatol

The planes in which the vectors of odourlessness, belonging to these odours, meet, have the form of a cone, respectively with the vector of valerian acid and that of scatol for their axis.

If we cast a glance at the sum of the results arrived at, it is especially the coincidence of several vectors at the same time which draws our attention: 4 vectors with regard to valerian acid and scatol, 4 sets of 3 vectors each time with regard to two others. Evidently there exists between the coinciding vectors agreement in action on our consciousness for those definite cases. But some of the coinciding vectors are repeatedly found together. Their mutual agreement must therefore be of a more intimate nature, otherwise it could not reveal itself so frequently and in so many different circumstances. This closer connection exists e.g. between isoamylacetate and nitrobenzol, which in no less than 4 cases become reciprocally identical to 1% of the circumference of the circle; a connection only a little less close between nitrobenzol and terpineol, nitrobenzol and guajacol and isamylacetate and guajacol, which do the same in 3 cases; a connection not quite wanting between isoamylacetate and terpineol and terpineol and guajacol, where also these appear to coincide to 1%.

But also the vectors with regard to which the coincidence of

several vectors comes about, are closely connected with each other. Valerian acid and scatol, with regard to which no less than 4 vectors become identical, have 4 mutual coincidences, to 1% and also the vectors with regard to which the coincidence of three vectors takes place, show in 3 cases out of 4, a plurality of identity. Considered from certain definite points of view, therefore, they must have something in common in their action upon our consciousness.

If we ask ourselves what physical importance the relations found might have, it must be this that odour-mixtures formed from the coinciding vectors possess fixants in common and these fixants will have to be found in the odour-classes to which the vectors with regard to which they are placed, belong. In perfumery are known a number of such fixants rendering useful services with regard to certain definite perfume-mixtures, which otherwise would not be durable. In my "Physiologie des Geruchs" I have given a series of such examples. Here we quote one borrowed from G. COHN's "die Riechstoffe". Artificial jasmin is obtained by joining together benzylacetate, linalylacetate, linalool and benzylalkohol, mixed with some indol, which serves "als Fixiermittel und zur Auffrischung des Geruchs", and which may be replaced by methylketol, scatol, propyldimethylindol, propylaethylindol, allylmethylindol, etc. With the aid of our table it must be possible to devise mixtures that will furnish available bouquets with fixants to be specified beforehand. Their practical fitness for the perfume-industry will depend, besides on the pure compensation-proportions, also on the velocity of evaporation and diffusion of the materials used. In a practically available perfume the latter should not differ too much.

The multidimensional character of the organ of smelling prevents, alas, projecting a clear representation of all proportions of the different qualities in their action upon consciousness. This is only partially possible, for separate vectors, isolated from the whole. Yet it appears that in general there exists a contrast between

isoamylacetate nitrobenzol terpineol guajacol	with regard to	aethylbisulfide valerian acid scatol

From a phylogenetic point of view the first group might be called the food-odours, the second the putrid odours, if not in many a case also muscon should be added to the last category, for which reason it is perhaps safer to refrain from any denomination. The arrangement in each group is governed by the above mentioned reciprocities.

Physiology. — "*A method to extract enzymes and pro-enzymes from the mucous membrane of the digestive tube and to establish the topic distribution of them.*" By Prof. H. J, HAMBURGER.

I. INTRODUCTION; PRINCIPLE OF THE METHOD.

The method applied as yet to extract enzymes and pro-enzymes from the mucous membranes of the stomach and the intestines consists in preparing the mucous membrane and extracting it in a fine state of division, with or without the addition of antiseptics; by repeated precipitation and dissolution the body to be examined is finally obtained in a more or less pure state. If we wish to be informed as to the distribution of the enzyme over the various parts of the mucous membrane, in other words to establish the topic distribution of it, extracts are made of equal weights or of equal surfaces, and of these the specific action is determined quantitatively.

It need hardly be said that these methods are rather complicated and lengthy as well. A great drawback more especially is, that in extracting, the enzyme is polluted with so many other substances of the mucous membrane.

Now, we have occupied ourselves for some time with the question by what force enzymes (pro-enzymes) are brought to the surface of the mucous membrane, and more especially tried to determine whether we have to do with kataphoresis, in other words whether in normal life enzymes (pro-enzymes) are carried along by the electric current arising when the secretory nerve fibres are stimulated in the natural way. [1]) We will not dwell on the results of these investigations now. Let us only observe here that the method consisted in laying on the mucous membrane a small column of solidified agar-agar, into which a platinum electrode had been melted; then it was investigated whether under the influence of a weak electric current, moving from the muscular side of the mucous membrane, to the free surface of it, enzyme or pro-enzyme passed from the epithelium cells into the agar agar.

That, if the enzyme or pro-enzyme was indeed moved by kataphoresis it would also pass into the agar-agar, we had a reason to expect after the investigations of GRAHAM [2]), VOIGTLÄNDER [3]) and others

---

[1]) HAMBURGER. Osmotischer Druck u. Ionenlehre. Bd. II. S. 433 ff.

[2]) GRAHAM, Liebig's Annalen **121**, 1862 S. 1.

[3]) VOIGTLÄNDER, Zeitschr. f. physik. Chemie. **3**, 1889 S. 316.

For the literature on this subject compare, COHEN, Vorträge für Aerzte über Physikalische Chemie 2e Aufl. 1907 S. 128.

according to which the velocity of diffusion in colloids is as great as in the water in which the colloid is dissolved.

If it should be objected that these experiments were made only with crystalloids, the investigations of C. EYKMAN [4]) have shown conclusively that colloids can diffuse into other colloids (gelatine into agar-agar).

But before trying to establish the influence of a constant electric current on the transition of enzyme into the agar-agar, we wished to know to what extent the ferment would diffuse into the agar-agar without the introduction of the electric current.

Evidently this transition took place. This fact seemed to suggest a means of extracting in an easy manner enzymes and perhaps pro-enzymes as well, from the mucous membrane in not too impure a state. Perfect extraction would, it is true, be unattainable in this way, but there was a likelihood that the method might be employed to determine in a simple manner the relative amounts of enzyme in the various parts of a mucous membrane.

II. EXPERIMENTAL METHOD.

Parts of a glass tube having in our experiments an internal diameter of 22 mm. and a height of 30 mm., were ground flat at one end by means of emery and placed with that side on a glass plate, plate glass being the best for this purpose.

By means of a pipette 3 cc. of liquid agar-agar were put into each little cylinder. I shall not discuss the way to prepare this liquid: it is to be found in all handbooks on the technics of bacteriology. It must be observed, however, that it is advisable to let the agar-agar solution cool down to $\pm$ 45° before measuring it in the pipette; otherwise there is a danger of its flowing partly away from underneath the glass cylinder.

After some time the agar colums have become solid and are placed, still surrounded by the glass tube, on the spread out parts of the membrane which, if necessary, has been previously cleaned. For this cleaning which also may serve to remove the mucus, we take NaCl 0,9%. Investigations especially made for this purpose on the gastric mucous membrane have shown, however, that for this organ at least washing with water gives satisfactory results.

On the mucous membrane, which if necessary has been cleaned, the agar-agar colums remain for 8 hours or more, in order to enable enzymes and pro-enzymes to diffuse into the agar-agar.

---

[4]) C. EYKMAN, Centralbl. f. Bakteriol. **29**, 1901, S. 841.

If the experiment bears upon the *pepsin incl. the pepsinogen of the gastric mucous membrane*, the agar columns which have been on it, are cut fine and mixed with 3 cc. HCl of 0.4%. For this we use cylindrical bottles with close fitting glass stoppers: they have a diameter of 24 mm. and a height of 48 mm. Into these bottles we put albumen columns prepared according to METT's method. When these have been in contact with the agar-suspension for 10 hours or more at 37.5 C., we determine by measurement how much has been digested; then the albumen columns are placed in it again and the measurements are repeated a few hours later. In each bottle we generally had two albumen tubes. Perhaps it will be objected that the presence of solid particles of agar-agar must impede the action of the pepsin on the albumen. This proves not to be the case: in the first place we observe that on all 4 sides of the 2 albumen columns always about the same column of albumen has been digested, which most likely would not be the case if now and then an agar-particle prevented the entrance of the digesting fluid. And secondly we noticed that when the experiment is made with a liquid, from which the agar particles have been removed by filtration, the rate of digestion is the same as when the agar particles were still in the fluid.

If the experiment bears only upon the *pepsinogen* of the gastric mucous membrane, we place alkalic instead of neutral agar-agar on it, viz. a quantity of agar of 2% in Na_2CO_3 of 3 p. mille. The investigations of LANGLEY[1]) have shown that in this concentration pepsin is decomposed by Na_2CO_3, pepsinogen on the other hand not.

It stands to reason that besides pepsin and pepsinogen, *chymosin* and *prochymosin* will also be absorbed by the neutral agar-agar. It was found indeed that the agar-mass had obtained the faculty of coagulating milk.

In a similar way as the gastric mucous membrane the intestinal mucous membrane may be experimented upon. We found that the neutral agar absorbs both enterokinase and erepsin. The quantity of *enterokinase* present in the agar is determined by cutting fine the agar, mixing it with water, *filtrating*, and bringing the extract thus obtained, into contact with inactive juice of a fresh pancreas gland and two albumen tubes.

The attentive reader will notice that here no agar particles are present at the digestion of the albumen as in the case of the gastric

---

[1]) LANGLEY Journal of Physiology **3** 1882 p. 253.
LANGLEY and EDKINS Ibid **7** 1886 p. 371.

juice. They were removed before the action of the fluid on the albumen tubes, because it was observed that the conversion of albumen by *trypsin* was greatly retarded by the presence of the agar-agar.

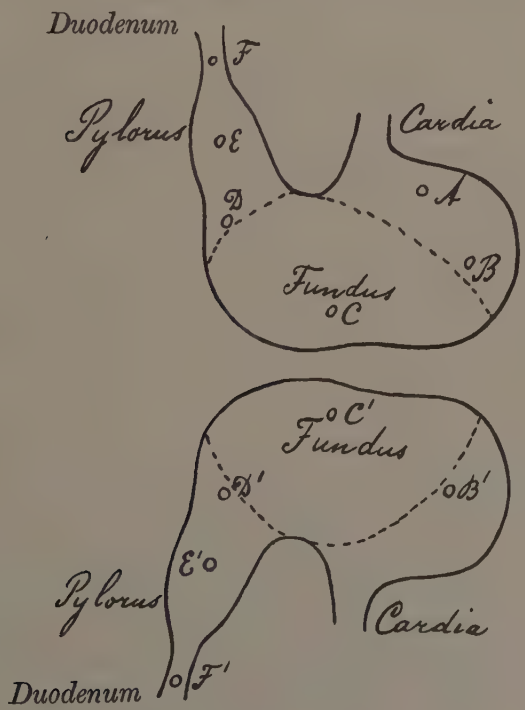
To determine the quantity of *erepsin*, drawn into the agar, we made the *clear* extract act upon the peptone.

We here append the results of some experiments carried out in accordance with the method described above. More explicit statements will be published elsewhere. Some further particulars concerning the method of investigation are mentioned below.

III. Some Experiments.

1. *Distribution of pepsin (incl. pepsinogen) over the gastric mucous membrane.*

A pig's stomach was cut into two symmetrical halves along the great and small curvature and washed with NaCl 0.9 %. Then both halves were spread out flat and on the spots marked below *A*, *B*, *C*, etc. columns of neutral agar-agar of 2 % were placed.



As will be seen *A* is situated in the cardea region.
B in the border region between cardea and fundus part
C in the fundus region
D in the border region between fundus and pylorus part
E in the pylorus region
F on the duodenum near to pylorus.

With respect to this figure we must point out that for *all* our experiments with gastric mucous membrane, the letters have the same meaning.

In the experiment of which table I gives the results, the agar columns of 3 cc. remained during $14^1/_2$ hours on the mucous membrane. Then the agar was cut fine and mixed with 3 cc 0.4 % HCl and each of the mixtures thus obtained was made to exert its digestive influence on two tubes of albumen.

The four numbers which in the following table are connected by + represent the lengths of the four albumen columns, digested at the 4 sides of the two tubes.

TABLE I.

Digested after $12^1/_2$ hrs.

A . . . . $^1/_2 + ^1/_2 + ^1/_2 + ^1/_2 = 2$ m.M.	*A'* . . . $^1/_2 + ^1/_4 + ^1/_2 + ^1/_2 = 1^3/_4$ m.M.
B . . . . $^3/_4 + ^3/_4 + ^1/_2 + ^3/_4 = 2^1/_4$ „	*B'* . . . $^3/_4 + ^3/_4 + ^3/_4 + ^3/_4 = 3$ „
C . . . . $2 + 2 + 2 + 2^1/_4 = 8^1{}_4$ „	*C'* . . . $2 + 2 + 2 + 2 = 8$ „
D . . . .$1^1/_2 + 1^1/_4 + 1^1/_2 + 1^1/_2 = 5^3/_4$ „	*D'* . . . $1^1/_2 + 1^1/_2 + 1^1/_2 + 1^1/_2 = 6$ „
E . . . .$1^1{}_4 + 1^1/_4 + 1^1/_2 + 1^1{}_4 = 5^1/_4$ „	*E'* . . . $1^1/_4 + 1^1/_4 + 1^1/_4 + 1^1/_2 = 5^1{}_4$ „
F . . . . $^1/_3 + ^1/_3 + ^1/_3 + ^1/_3 = 1^1/_3$ „	*F* . . . $^1/_3 + ^1/_3 + ^1/_3 + ^1/_2 = 1^1/_3$ „

From this table is seen:

1. *That in the cardia region* (*A and A'*) *the amount of pepsin is small, increases towards the fundus* (*B and B'*), *reaches its climax there* (*C and C'*) *and decreases towards the pylorus* (*D and D'*). *In the duodenum we also meet with pepsin, but its quantity is small.*

2. The table shows that in both halves of the stomach the quantity of pepsin was equal in corresponding parts.

If we speak here of pepsin we mean pepsin and pepsinogen. As has been said before and will further be demonstrated pepsinogen

too enters the agar. It is by mixing with HCl converted into pepsin and so determined quantitatively with the pepsin.

2. *Distribution of pepsinogen.*

As has been said, the investigations of LANGLEY [1]) have shown that, contrary to pepsin, pepsinogen is not destroyed by a solution of Na_2CO_3 0.3%. We have made use of this fact to try if we could withdraw pepsinogen from the mucous membrane.

For this purpose agar columns were placed upon the mucous membrane containing 2% of agar in a Na_2CO_3 solution of 0.3%. The column again had a diameter of 22 mM., the contents being 3 cc.

It must be casually observed that separate experiments had shown that in such an alkalic agar mass, pepsin at once loses irretrievably its digestive power.

To the method of experimenting we have not much to add. Let us only mention that the alkalic agar, after having been in contact with the mucous membrane was cut fine, neutralized with diluted hydrochloric acid, then mixed with 3 cc. HCl of 0.4%. The purpose of this was, to liberate the pepsin from the pepsinogen. The digesting-experiments with albumen-tubes gave the results tabulated below. Here the lengths of the 4 digested albumen columns have each time been added together.

TABLE III.

The agar columns were kept on the mucous membrane for 20 hours.

Digestion of albumen after 8 hours.	Digestion of albumen after 18 hours.
A . . . 0 m.M.; *A'* . . . 0 m.M.	*A* . . . 0 m.M.; *A'* . . . 0 m.M.
B . . . 0 „ ; *B'* . . . 0 „	*B* . . . 1½ „ ; *B'* . . . 1½ „
C . . . 8 „ ; *C'* . . . 8 „	*C* . . . 10 „ ; *C'* . . . 9½ „
D . . . 4.4 „ ; *D'* . . . 4.2 „	*D* . . . 6.2 „ ; *D'* . . . 6.9 „
E . . . 4 „ ; *E'* . . . 4 „	*E* . . . 5 „ ; *E'* . . . 5.2 „
F . . . 0 „ ; *F'* . . . 0 „	*F* . . . 1 „ ; *F'* . . . 1 „

It will be seen *that from the cardea part* (*A* and *A'*) *no pepsinogen was extracted.* This need not surprise us; for in several experiments with *neutral* agar, no pepsin could be extracted from it either.

In the border region between cardea and fundus, pepsinogen was found, but in a small quantity. It was considerable in the fundus (C), gradually growing less towards the pylorus (D and *E).*

[1]) LANGLEY, l. c.

3. *To what extent does the length of time during which the agar columns are on the mucous membrane, influence the quantity of enzyme and pro-enzyme absorbed?*

For these experiments the stomach was divided into two symmetrical halves. On one half two *neutral* agar-columns were placed at *A*, *B*, *C* etc., and on the corresponding places of the other half *A'*, *B'*, *C'* etc. two columns of *alkalic* agar. One of the two columns near *A*, near *B*, near *C* etc. was taken away and treated, after having been on the mucous membrane for 18 hours; the same was done with those near *A'*, *B'*, *C'* etc. The other series *A*, *B*, *C* etc. *A'*, *B'*, *C'* etc. was left on the membrane for 36 hours. In both series of experiments the thus activated agar was made to act for 20 hours on the albumen columns. The tables will be plain now without further explanation.

TABLE IV.

Determination of the quantity of pepsin and pepsinogen which had passed into the neutral agar, after the latter had been on the mucous membrane for

	18 hours	36 hours
A	0 m.M. digested	2⅓ m.M. digested
B	1 „ „	3½ „ „
C	4.8 „ „	16 „ „
D	3.4 „ „	7 „ „
E	3 „ „	5.4 „ „
F	0 „ „	2 „ „

TABLE V.

Determination of the quantity of pepsinogen which had passed into the alkalic agar, the latter having been on the mucous membrane during

	18 hours	36 hours
A'	0 m.M. albumen digested	1½ m.M. albumen digested
B'	0 „ „ „	2¼ „ „ „
C'	3.8 „ „ „	10 „ „ „
D'	2.4 „ „ „	5½ „ „ „
E'	1.2 „ „ „	3 „ „ „
F'	0 „ „ „	1 „ „ „

Both tables show that after 36 hours more pepsin and also more pepsinogen had passed into the agar than after 18 hours.

Further a comparison of tables IV and V makes it evident that the digestion of albumen in experiments made with neutral agar, is more considerable than where alkalic agar has been employed. This result may also tend to confirm the reliability of the method; for into the neutral agar pepsin and pepsinogen may enter, the latter of which under the influence of hydrochloric acid produces pepsin, whilst in the alkalic agar only pepsinogen is found. And as we have seen invariably in all our experiments, the quantity of enzyme and pro-enzyme at identical spots of the two symmetrical parts of the stomach turns out to be the same.

I wish to observe here that the digestion of serum-albumen takes place much more quickly than that of the egg-albumen used. GLÄSSNER was the first to point out the advantage of coagulated serum, and I may confirm it from my own experience. Serum albumen has moreover the advantage that without preparation such as cutting up and filtrating, it can be used after simply being coagulated in glass tubes.

Owing to accidental circumstances no serum-albumen has been used for the experiments described in this paper.

4. *Distribution of rennet-ferment.*

To demonstrate the presence of rennet-ferment and to know its distribution in the gastric mucous membrane, about the same method was applied as that used for the investigations relating to pepsin and pepsinogen. Only the agar-columns had a greater diameter than in the pepsin experiments, viz. 35 instead of 22 mM. The contents accordingly were 5 cc. instead of 3 cc. Moreover it was self-evident that the quantitative determination of the rennet-ferment had to be effected in another way. The columns having been on the mucous membrane for some hours, the agar was cut fine and mixed in a test-tube with $^1/_2$ cc. HCl 0.4% and afterwards with 10 cc. of milk. Then the test tube was plunged into a bath of water at 37.5°, after which it was noted down every half minute where coagulation had taken place.

The presence of some hydro-chloric acid did not impair the experiment. Previous tests had shown that in a mixture of 5 cc. neutral agar $^1/_2$ cc. HCl of 0.4% and 10 cc. of milk coagulation did not set in till more than an hour after. As the following series of experiments demonstrates the addition of only $^1/_2$ cc. of HCl can hardly

have had any influence of the coagulative action of the rennet-ferment.

TABLE VI.

Coagulation is visible:

by	*A*	after 3 minutes;		by	*A'*	after 3 minutes.	
„	*B*	„ 2	„	„	*B'*	„ 2	„
„	*C*	„ 1	„	„	*C'*	„ 1	„
„	*D*	„ 1½	„	„	*D'*	„ 1½	„
„	*E*	„ 2½	„	„	*E'*	„ 2½	„

This experiment shows that the distribution of chymosin (including pro-chymosin) runs parallel with that of pepsin (including pro-pepsin), a result agreeing with the researches of others.[1])

Secondly the experiment shows the action of the rennet in corresponding parts of the two symmetrical halves of the stomach to be equal.

5. *Distribution of enterokinase in the intestinal mucous membrane.*

On the mucous membrane of the duodenum, jejunum, ileum, coecum and colon, cut open length-wise,agar-columns were placed, their contents being 3 cc. These having been left on it for 24 hours, the agar-agar was cut fine and extracted with 3 cc. of a Na Fl-solution of 2 %. Then 6 cc. of diluted pancreatic juice were added to 2 cc. of the filtrate. The former had been obtained by pressing the pancreas gland of a newly killed pig, mixing the thick juice thus obtained with a Na Fl-solution of 2 %, and filtrating the mixture.

In the mixture of 6 cc. diluted pancreatic juice thus obtained and 2 cc. agar-filtrate two albumen tubes were placed.

By the side of this, controlling-experiments were made with 2 cc. agar-filtrate and 6 cc. of Na Fl solution, instead of 6 cc. of the diluted pancreatic juice. The digestion of the albumen was noted down after 19 and 44 hours.

---

1) Nencki u. Sieber. Zeitschr. f. physiol. Chemie **32** 1901 S. 291; Pekelharing. Ibid. **35** 1902 S.8; Pawlow u. Parastschuk. Ibid **42** 1904 S. 415; Sawjalow. Ibid **46** 1905 S. 307.

The following table gives the results of one of the series of experiments made.

TABLE VII.

	2 cc duodenum-agar extract		2 cc jejunum-agar extract		2 cc ileum-agar extract	
	+ 6 cc pancreatic juice	+ 6 cc NaFl. solution	+ 6 cc pancreatic juice	+ 6 cc NaFl. solution	+ 6 cc pancreatic juice	+ 6 cc NaFl. solution
Albumen digested after 19 hours	7.2 m.M.	0 m.M.	6.4 m.M.	0 m.M.	5.6 m.M.	0 m.M.
Albumen digested after 44 hours	12.4 „	0 „	11.2 „	0 „	10 „	0 „

This series of experiments shows *the quantity of enterokinase to decrease gradually downward, a result agreeing with that obtained by* Chepowalnikow, Delezenne, Frouin *and* Falloise.

I shall not discuss the experiments here, which show that in the digestion of albumen by trypsin the presence of agar has a retarding influence, nor the influence which the time during which the agar has been in contact with the intestinal mucous membrane, has on the transition of the enterokinase. These questions will be further discussed in a more explicit account.

One experiment remains to be mentioned, showing how the enterokinase diffused into the agar, distributes itself over agar and water, after the agar has been cut up and mixed with water.

5 cc. of liquid agar are mixed with 2 cc. of watery extract of the intestinal mucous membrane. Of this mixture 2×3 cc. are taken and poured into the above mentioned cylindrical tubes. When the agar has become solid it is cut fine and mixed each time with 2 cc. of water. The mixture remains for an hour exposed to the temperature of the body in order to enable the agar to give up enterokinase.

After cooling down it is filtrated, twice 1 cc. is taken and mixed with 2 cc. of inactive pancreatic juice. In both mixtures I and II albumen tubes are placed.

Besides this experiment another one identical with it, is made; only instead of 5 cc. of agar, 5 cc. of water are taken of course. Cutting up is out of the question here. The quantities, however, remain the same.

TABLE VIII.

Liquid	Digestion after	Experiment I	Experiment II
5cc agar+2cc intest. extr.; of this 2×3 cc cut up; each 3 cc mixed with 2 cc water; of this 2×1 cc mixed each with 2 cc pancreatic juice	4 hours	1 + 1 + 1 + 1 = 4 m.m.	1 + 1 + 1 + ¾ = 3¼ m.m.
	16 hours	3½ + 4½ + 3½ + 4 = 15½ m.m.	3½ + 3½ + 3½ + 4 = 14½ m.m.
	25 hours	6 + 5 + 6 + 5 = 22 m.m.	5 + 5 + 6 + 5 = 21 m.m.
5 cc water + 2cc intest.extr. of this 2×3 cc; each 3 cc mixed with 2 cc of water; of this 2×1 cc mixed each with 2 cc of pancreatic juice.	4 hours	1¼ + 1¼ + 1 + 1 = 4½ m.m.	1¼ + 1 + 1½ + 1¼ = 5 m.m.
	16 hours	4 + 4½ + 4 + 4 = 16½ m.m.	4 + 3½ + 4 + 4½ = 17 m.m.
	25 hours	6 + 5 + 5 + 6 = 22 m.m.	5 + 5 + 5 + 6 = 21 m.m.

This table leaves no doubt, but the method of extracting the agar with water, gives reliable results. *They turn out to be the same as if the agar itself were water. The enterokinase must distribute itself equally over agar and water.*

We observed the same with pepsin.

Finally we shall describe a series of experiments, showing that erepsin too enters the agar, and that this supplies us with a means of determining its distribution over the intestinal mucous membrane.

6. *Distribution of Erepsin.*

The 2% agar used was not dissolved in water, but in NaFl of 2% because the amount of erepsin, passing from the intestine into the agar during the time taken up by the former experiments, was not great enough.

Therefore it was expedient to leave the agar for at least 24 hours on the mucous membrane, taking care to prevent putrefaction as much as possible.

The action of erepsin consists as we know in its power to change hemialbumose and peptone into products not giving the biuret-reaction.

VERNON [1]) has based on this a colorimetric method, to determine the degree of conversion brought about by erepsin and FALLOISE [2]) among others, has successfully used it. We too have applied this method, in a somewhat modified form, however. It chiefly consisted in a solution of $CuSO_4$ being mixed with a NaOH solution. The fluid thus obtained imparts a violet-red colour to peptone. The more the peptone solution from which we started is converted by erepsin, the fainter the violet-red colour will be. It was now investigated, with how much water the standard liquid had to be diluted to produce the violet-red colour observed.

One of our experiments gave the following result.

In the peptone-solution (WITTE) on which the duodenal-extract has acted, are **46.2**% of the original quantity of peptone left. In the peptone-solution acted upon during the same time by the *jejunum*-agar-extract are still **16**% of the original quality of peptone left, and lastly where the *ileum*-agar-extract acted during the same time, **14**% of the original amount.

It follows from this that in jejunum and ileum there was more erepsin present than in duodenum, which corroborates so far FALLOISE's results inasmuch as we too found much more erepsin in jejunum than in duodenum. In the ileum, however, the amount of erepsin is much greater than in the duodenum; FALLOISE, indeed, notes a difference in the same direction, but it is only slight. It must be kept in mind though, that our experiments relate to the pig, FALLOISE's to the dog.

I may add that in PEYER's plâques hardly ány erepsin or enterokinase was found.

A number of experiments, made for the researches described above, have been carried out by Mr. R. A. B. OOSTERHUIS, Med. cand., assistant at the physiological laboratory.

CONCLUSION.

The above researches have shown:

1. That when agar columns are placed upon the mucous membrane of stomach and intestines, enzymes and pro-enzymes are

[1]) VERNON. Journal of Physiology. **30**, 1903, p. 330.

[2]) FALLOISE. Archives internat. de Physiol. **2**, 1903/4, p. 299.

absorbed from them and enter the agar. As such were examined pepsin, including pepsinogen, chymosin and prochymosin, enterokinase and erepsin.

2. The above-mentioned ferments can be extracted, partly at least, by water from the agar-agar. Quantitative investigations have shown even that pepsin + pepsinogen and enterokinase as well, distribute themselves equally over the agar and water.

3. The facts mentioned sub 1 and 2 suggest a simple means of extracting the above-named ferments from the mucous membrane, and of determining quantitatively the distribution of them.

We have only to leave solid agar-agar columns of equal dimensions on various parts of the mucous membrane for some time and make subsequently a comparative quantitative determination of the specific action of the watery agar extract.

4. The results obtained with this new method with respect to the distribution of the above-named ferments in the digestive tube of the pig confirm those obtained by most investigators with the usual extraction methods on the dog.

5. The advantages of the method over the usual one consist, besides in its greater simplicity, also in the fact that the enzyme under investigation is much less polluted by decomposition products of the mucous membrane.

Especially for the investigation of the distribution of enzymes in individuals who, when alive suffered from diseases of the stomach or intestinal canal (ulcers in the stomach, the intestines, etc.) the method seems to me likely to be of use.

Moreover it is to be expected that besides the ferments examined till now, others will also pass into the agar-agar, which will enable us to make quantitative determinations of them in a similar way.

Finally the method seems to me to deserve recommendation as it can be applied in experiments at a lecture; at the same time, by adding congo-red or a similar indicator to the agar, the amount of acid or alkali can be demonstrated ocularly.

Groningen, September 1907.

Mathematics. — "*The extension of the Configuration of* KUMMER *to spaces of* (2^p-1) *dimensions.*" By Mr. J. A. BARRAU. (Communicated by Prof. D. J. KORTEWEG.)

(Communicated in the meeting of September 28, 1907).

§ 1. If we represent by S_1 the system $\begin{matrix} a & b \\ b & a \end{matrix}$, built up out of two letters and by S_2 the same system in new letters c and d; if likewise we represent by T the system of signs $\begin{matrix} + & + \\ + & - \end{matrix}$ and by $-T$ the opposite $\begin{matrix} - & - \\ - & + \end{matrix}$, we obtain by connecting these

$$\begin{matrix} S_1 & S_2 \\ S_2 & S_1 \end{matrix} \quad \text{and} \quad \begin{matrix} T & T \\ T & -T \end{matrix}$$

the two systems

$$\begin{matrix} a & b & c & d \\ b & a & d & c \\ c & d & a & b \\ d & c & b & a \end{matrix} \quad \text{and} \quad \begin{matrix} + & + & + & + \\ + & - & + & - \\ + & + & - & - \\ + & - & - & + \end{matrix}$$

By giving *each* row of four letters in turn the signs of *each* row of the system of signs sixteen quadruplets of algebraic quantities appear which, as is known [1]), represent the elements of the $Cf(16_8)$ of KUMMER whether they are considered as homogeneous coordinates of points or as coefficients of planes in Sp_3. For, to each element are incident the elements of another kind, represented by the three permutated letter quadruplets and for each of them with half of the sign combinations.

§ 2. If now we call S_1 and T the letter- and the sign-system of 4 resp. and if we repeat the combination described above suchlike systems of 8 are formed of which that one of the letters furnishes the permutations of a *regular* G_8 of order 8 [2]), consisting exclusively of binary substitutions, whilst that of the signs is *anallagmatic* [3]), i. e. every two rows show as many sign variations as

---

[1]) See a.o. JESSOP *Line-Complex* p. 23 or HUDSON *Kummer's Surface* p. 5.

[2]) Compare MILLER *Quart. Journ.* 28 p. 255, group 8 No. 4.

[3]) LUCAS *Récréations Mathématiques* II p. 113; *Nieuw Archief voor Wiskunde* 7 p. 256.

sign-permanencies. The systems become (that of the signs somewhat differently arranged):

I	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*
II	*b*	*a*	*d*	*c*	*f*	*e*	*h*	*g*
III	*c*	*d*	*a*	*b*	*g*	*h*	*e*	*f*
IV	*d*	*c*	*b*	*a*	*h*	*g*	*f*	*e*
V	*e*	*f*	*g*	*h*	*a*	*b*	*c*	*d*
VI	*f*	*e*	*h*	*g*	*b*	*a*	*d*	*c*
VII	*g*	*h*	*e*	*f*	*c*	*d*	*a*	*b*
VIII	*h*	*g*	*f*	*e*	*d*	*c*	*b*	*a*

1	+	+	+	+	+	+	+	+
2	+	+	+	+	−	−	−	−
3	+	+	−	−	+	+	−	−
4	+	−	+	−	+	−	+	−
5	+	−	−	+	−	+	+	−
6	+	−	−	+	+	−	−	+
7	+	−	+	−	−	+	−	+
8	+	+	−	−	−	−	+	+

By providing each of the rows of letters with each of the sign-combinations there appear sixty-four octuples of algebraic numbers to which we assign the notations I 1, I 2, ... VIII 8. Whether we consider these numbers as homogeneous coordinates of points or as coefficients of equations of Sp_6 in a Sp_7, each element is incident to $7 \times 4 = 28$ of another sort, namely to half of the sign combinations of each letter permutation; so a *Cf.* (64_{28}) appears, to be designated by K^{VII}.

As with K^{III} it is possible to combine the *Cf*-elements to simplexes *A*, *B*, *C*, *D*, *E*, *F*, *G*, *H* in various ways. Such an arrangement is i. a.:

	1	2	3	4	5	6	7	8
A	I 1	II 4	III 5	IV 3	V 7	VI 8	VII 6	VIII 2
B	I 2	II 7	III 6	IV 8	V 4	VI 3	VII 5	VIII 1
C	I 3	II 6	III 7	IV 1	V 5	VI 2	VII 4	VIII 8
D	I 4	II 1	III 8	IV 6	V 2	VI 5	VII 3	VIII 7
E	I 5	II 8	III 1	IV 7	V 3	VI 4	VII 2	VIII 6
F	I 6	II 3	III 2	IV 4	V 8	VI 7	VII 1	VIII 5
G	I 7	II 2	III 3	IV 5	V 1	VI 6	VII 8	VIII 4
H	I 8	II 5	III 4	IV 2	V 6	VI 1	VII 7	VIII 3

The table indicates that eight vertices of e.g. the simplex *A* are resp. the points I 1, II 4 etc, according to the former notation, whilst at the same time the eight opposite side-Sp_6 of the simplex are represented by those same notations.

The connection of Cf-elements can now be represented by a diagram (pl. I) the rows of which indicate the Sp_6, the columns the points, whilst incidence of a Sp_6 with a point is indicated by hatching the square common to the respective row and column.

We see that the diagram can be brought to a more condensed shape:

	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*
A	*S*	*a*	*b*	*c*	*d*	*e*	*f*	*g*
B	*a*	*S*	*g*	*f*	*e*	*d*	*c*	*b*
C	*b*	*g*	*S*	*e*	*f*	*c*	*d*	*a*
D	*c*	*f*	*e*	*S*	*g*	*b*	*a*	*d*
E	*d*	*e*	*f*	*g*	*S*	*a*	*b*	*c*
F	*e*	*d*	*c*	*b*	*a*	*S*	*g*	*f*
G	*f*	*c*	*d*	*a*	*b*	*g*	*S*	*e*
H	*g*	*b*	*a*	*d*	*c*	*f*	*e*	*S*

Here S indicates a simplex-filling; each of the other letters a system (8_8) denoting the incidence connection between the elements of two simplexes. These systems (8_8) have all degenerated into two (4_8), each pair of our simplexes is thus connected in an equal way and forms a $Cf(16_{10})$ of the same type.

§ 3. Analogous to the well-known decomposition of K^{III} into four tetrahedra lying in pairs in a MÖBIUS-position, it is obvious to call the position of two of the simplexes, e. g. A and B, by that name. Each side-Sp_6 of one S contains three points, so a face, of the other; each vertex of one lies in three side-Sp_6, so in a side-Sp_4 of the other; the correspondence is such that opposite elements of A_1 e.g. vertex A_1 and side-space A_1 also furnish opposite elements of B, namely resp. the side-Sp_4: $B_1B_5B_6B_7B_8$ and the face $B_2B_3B_4$, just as this is the case with the tetrahedra in MÖBIUS-position.

There exists already however, provided with the same property, an extension of this notion, that of BERZOLARI [1]) where each side-Sp_6 of one S contains one vertex of the other, and is generated by operation with a focal system on an arbitrary simplex; let us call this position $M\,I$, then it is evident that the discussed more specialized $M\,II$ is to be regarded as a threefold $M\,I$.

[1]) *Rendiconti del Circolo Matem. di Palermo* 22.

The elements of two simplexes A and B in $M\,II$ can be arranged only in one other way to two suchlike simplexes, namely as

first simplex P: $A_1, A_2, A_3, A_4, B_5, B_6, B_7, B_8$,
second „ Q: $B_1, B_2, B_3, B_4, A_5, A_6, A_7, A_8$.

If we regard such a new simplex in connection with $C, D, \ldots H$, it then shows with each of these a new sort of position; for all however of the same type, showing analogy to the pairs of tetrahedra in STEINER-position which can be separated in the same way from K^{III} [1]). We find for the $cf\,(16_{10})$ of two such simplexes a diagram of the shape:

$$\begin{matrix} S & x \\ x & S, \end{matrix}$$

where x again represents a system (8_3) which however does not degenerate now, but is identical to the cyclic system which is obtained out of the initial row: 1 2 . . 5 . . .

Opposite elements of one simplex furnish, as in Sp_3, no opposite ones of the other.

§ 4. The 28 operations determining in each cf-space the cf-points incident to them and reciprocally, are *focal-correlations*; thus e.g. the $Sp_6 : A_1$

$$(+a, +b, +c, +d, +e, +f, +g, +h)$$

is transformed into the point A_2 situated in it

$$(+b, -a, +d, -c, +f, -e, +h, -g)$$

by operating with the skew-symmetrical determinant of transformation:

$$\begin{vmatrix} 0 & +1 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & +1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & +1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & +1 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \end{vmatrix}$$

These focalsystems are mutually in involution as the group of the letter substitutions as well as that of the sign variations are ABEL groups.

The 36 remaining reciprocities are polarities with respect to some 36 quadratic Sp_6, which serve for K^{VII} as the 10 fundamental-surfaces of order two for K^{III}.

---

[1]) MARTINETTI, *Rendic. Palermo* 16 p. 196.

Their equations are of two types; namely *eight* of the form

$$\pm x_1'^2 \pm x_2^2 \pm x_3^2 \pm x_4^2 \pm x_5^2 \pm x_6^2 \pm x_7^2 \pm x_8^2 = 0,$$

where the combinations of signs must be derived from the sign system; and twenty-eight of the form:

$$\pm x_1 x_2 \pm x_3 x_4 \pm x_5 x_6 \pm x_7 x_8 = 0,$$

where the connection of the indices is given by the seven binary substitutions of the regular G_8, whilst the signs must be selected:

$$\begin{array}{cccc} + & + & + & + \\ + & + & - & - \\ + & - & + & - \\ + & - & - & + \end{array}$$

The sixty-three operations which transform an element into another of the same sort are *collineations*; so we obtain, analogous to the KLEIN G_{32} in Sp_3, *a geometrical* ABEL *group* G_{128}, *consisting of the identity and sixty-three collineations; twenty-eight focal systems in involution and thirty-six polarities.*

§ 5. *The twenty-eight points in each* Sp_6 *of* K^{VII} *lie on a quadratic* Q_5 *and reciprocally.*

To prove this we regard the determinant of the terms of order two, formed of seven of the eight homogeneous coordinates; so this is of order $7 + \binom{2}{7} = 28$. The omission of a coordinate is geometrically the projecting out of a vertex of the fundamental simplex on the opposite Sp_6; if the projections of 28 points lie in it quadratically, then the points themselves do so in their Sp_6.

Let us first restrict ourselves to $Sp_6 : A_1$.

The twenty-eight points are to be divided into seven quadruplets of the same order of letters; the purely quadratic terms within such a quadruplet are in each column alike, the mixed ones may differ in sign. Let us call the four terms in a column p, q, r, s, then the substitution

$$\begin{array}{l} P = p + q + r + s \\ Q = p + q - r - s \\ R = p - q + r - s \\ S = p - q - r + s \end{array}, \text{ the } \Delta \equiv \begin{vmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 \end{vmatrix} \text{ of which is } \neq 0,$$

causes three of the four quadratic terms to disappear, the Δ_{28} breaks up into the product of a Δ_7 of quadratic and a Δ_{21} of mixed terms. Here

$$\Delta_7 = \begin{vmatrix} b^2 & a^2 & d^2 & c^2 & f^2 & e^2 & h^2 \\ c^2 & d^2 & a^2 & b^2 & g^2 & h^2 & e^2 \\ d^2 & c^2 & b^2 & a^2 & h^2 & g^2 & f^2 \\ e^2 & f^2 & g^2 & h^2 & a^2 & b^2 & c^2 \\ f^2 & e^2 & h^2 & g^2 & b^2 & a^2 & d^2 \\ g^2 & h^2 & e^2 & f^2 & c^2 & d^2 & a^2 \\ h^2 & g^2 & f^2 & e^2 & d^2 & c^2 & b^2 \end{vmatrix}$$

That in general $\Delta_7 \neq 0$ is evident i. a. from

$$h = 1 \ , \ a = b = c = d = e = f = g = 0.$$

The Δ_{21} gets after change of signs of some rows the form:

0	0	0	0	0	bh	0	0	0	0	$-ah$	0	df	$-de$	0	$-cf$	ce	0	0	0	0
0	0	0	bf	$-be$	0	0	0	$-af$	ae	0	0	0	0	dh	0	0	$-ch$	0	0	0
0	bd	$-bc$	0	0	0	$-ad$	ac	0	0	0	0	0	0	0	0	0	0	0	fh	$-e$
0	0	0	0	ch	0	0	0	dg	0	$-de$	0	0	$-ah$	0	$-bg$	0	be	0	0	0
0	0	0	cg	0	$-ce$	0	0	0	dh	0	0	$-ag$	0	ae	0	$-bh$	0	0	0	0
$-cd$	0	bc	0	0	0	ad	0	0	0	0	$-ab$	0	0	0	0	0	0	$-gh$	0	eh
0	0	0	dh	0	0	0	0	0	cg	$-cf$	0	0	$-bg$	bf	$-ah$	0	0	0	0	0
0	0	0	0	dg	$-df$	0	0	ch	0	0	0	$-bh$	0	0	0	$-ag$	af	0	0	0
cd	$-bd$	0	0	0	0	0	$-ac$	0	0	0	ab	0	0	0	0	0	0	gh	$-fh$	0
0	0	$-eh$	0	0	0	$-fg$	0	0	0	cf	0	0	bg	0	ah	0	0	0	0	$-b$
0	$-eg$	0	0	0	ce	0	$-fh$	0	0	0	0	ag	0	0	0	bh	0	0	$-ac$	0
$-ef$	0	0	0	be	0	0	0	af	0	0	$-gh$	0	0	0	0	0	ch	$-ab$	0	0
0	$-fh$	0	0	0	0	0	$-eg$	0	0	de	0	0	ah	0	bg	0	0	0	$-bd$	0
0	0	$-fg$	0	0	df	$-eh$	0	0	0	0	0	bh	0	0	0	ag	0	0	0	$-a$
ef	0	0	$-bf$	0	0	0	0	0	$-ae$	0	gh	0	0	$-dh$	0	0	0	ab	0	0
$-gh$	0	0	0	0	0	0	0	0	0	ah	$-ef$	0	de	0	cf	0	0	$-cd$	0	0
0	0	fg	0	$-dg$	0	eh	0	$-ch$	0	0	0	0	0	0	0	0	$-af$	0	0	ad
0	eg	0	$-cg$	0	0	0	fh	0	$-dh$	0	0	0	0	$-ae$	0	0	0	0	ac	0
gh	0	0	0	0	$-bh$	0	0	0	0	0	ef	$-df$	0	0	0	$-ce$	0	cd	0	0
0	fh	0	0	$-ch$	0	0	eg	$-dg$	0	0	0	0	0	0	0	0	$-be$	0	bd	0
0	0	eh	$-dh$	0	0	fg	0	0	$-cg$	0	0	0	0	$-bf$	0	0	0	0	0	bc

The sum of the numbers in each column amounts to zero; so

$$\Delta_{21} = 0.$$

As each element with the 28 incident to it can be transformed into any other by means of a direct or reciprocal projectivity, the quadratic position of every 28 is now proved.

§ 6. Each couple of Sp_6 of the cf has twelve points in common lying thus in a Sp_5. No other Sp_6 containing these twelve, all these Sp_5 differ and their number is $\binom{2}{64} = 2016$. The cf-points form with them a cf $(64_{378}, 2016_{12})$.

There are triplets of Sp_6 which have six points in common, lying thus in a Sp_4, each cf-Sp_5 has namely in still 32 Sp_6 *six* of its points. Such a sextuple can be deduced from three groups of twelve, their number is thus $\frac{2016 \times 32}{3} = 21504$; they form with the cf-Sp_5 a cf $(21504_3, 2016_{32})$.

There are quadruplets of Sp_6 having four points in common which therefore determine a Sp_3; each cf-Sp_4 has namely four of its six points in fifteen other cf-Sp_6. Every Sp_3 can be derived from four Sp_4, their number is thus $\frac{21504 \times 15}{4} = 80640$. They form with the cf Sp_4 a cf $(80640_4, 21504_{16})$.

There are sextuplets of Sp_6 having three points of the cf in common, which therefore determine a Sp_2; each cf-Sp_3 has namely three of its four points in eight other cf-Sp_6 more, these eight Sp_6 furnish two by two however the same triplet; as furthermore each Sp_2 can be deduced from $\binom{2}{6} = 15$ Sp_3 their number is $\frac{80640 \times 4}{15} = 21504$. This could be expected as the whole consideration starting from the cf-points might have been put reciprocally, and would then have led on account of the self-reciprocity of the system to the same elements; so still 2016 Sp_1 are obtained, the right lines of connection of the pairs of points.

The further amounts of incidences of the kinds of elements mutually can now be easily deduced; the notation of K^{VII} becomes finally:

	Sp_0	Sp_1	Sp_2	Sp_3	Sp_4	Sp_5	Sp_6
	64	2016	21504	80640	21504	2016	64
incident to:							
Sp_0	—	2	3	4	6	12	28
Sp_1	63	—	3	6	15	66	378
Sp_2	1008	32	—	4	21	160	2016
Sp_3	5040	240	15	—	15	240	5040
Sp_4	2016	160	21	4	—	32	1008
Sp_5	378	66	15	6	3	—	63
Sp_6	28	12	6	4	3	2	—

By the method of intersecting and projecting triplets and doublets of consecutive kinds of elements are to be transformed into elements of Sp_3 or Sp_2; thus are formed e.g. a *cf* $(21504_{,1})$ of points and planes, with 80640 *cf*-lines; and a plane *cf* $(2016_{,,}, 21504_{,})$ of points and lines, or reciprocally.

§ 7. If we represent the system of letters and that of signs of 8 resp. by S_1 and T and if we repeat the combination

$$\begin{matrix} S_1 & S_2 \\ S_2 & S_1 \end{matrix} \quad \text{and} \quad \begin{matrix} T & T \\ T & -T, \end{matrix}$$

we obtain systems for 16 belonging to each other, etc., the operation allowing of indefinite continuation; one always arrives at a regular ABEL substitution group G_{2^p} and a suitable anallagmatical system for the signs.

These always furnish in R_{2^p-1} a *cf*, analogous to that of KUMMER with the notation:

$$Cf\left(2^{2p}_{(2^p-1).\,2^{p-1}}\right),$$

arising from an arbitrary starting element by an operation with a geometrical ABEL group:

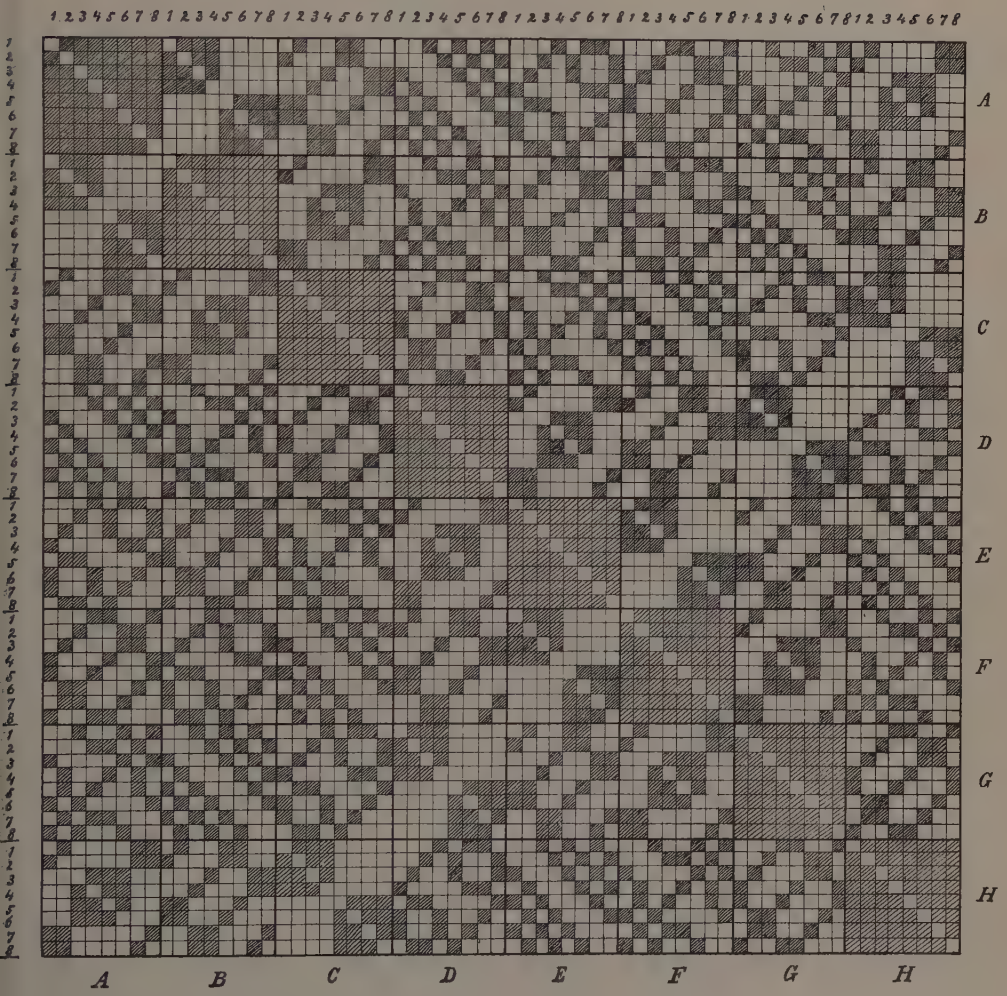
the *identity* and $2^{2p}-1$ *collineations* on one hand

and $(2^p-1).2^{p-1}$ *focal systems* mutually in involution with $(2^{p+1}-2^p+1).2^{p-1}$ *polarities* on the other hand.

The quadratic situation of the elements incident to one element can always be proved by reduction of the determinant according to the example of § 5 [1]).

[1]) A more extensive treatment also for spaces of other numbers of dimensions will follow in the dissertation to be published: J. A. BARRAU, *Bijdragen tot de theorie der cff.* (Amsterdam 1907).

J. A. BARRAU. "Analogon of the configuration of KUMMER in Sp_7."



Mathematics. — *"The theorem of* GRASSMANN *in a space of n dimensions."* By LUCIEN GODEAUX, at Morlanwelz (Hainault). (Communicated by Prof. P. H. SCHOUTE).

We shall designate by the letter S a linear space and the number of dimensions of this space shall be the index.

The notation V_i^j represents a variety, the locus of ∞^i elements and of order j.

The order of a variety, locus of spaces S_k occurring in an $(n-k)(k+1)-1$ times infinite number in a space S_n, is the number of S_k of an S_{k+1} through an S_{k-1} of this S_{k+1} and belonging to the variety.

1. In an S_2 the theorem of GRASSMANN can be read thus:

The locus of S_0 for which the S_1 which unite it to three fixed S_0 meet three fixed S_1 in three S_0 of the same S_1 is a variety V_1^3.

In an S_3 it has been given it the two following forms:

The locus of an S_0 for which the S_2 which unite it to four fixed S_1 meet four fixed S_1 in four S_0 of a same S_1 is a V_2^4. (LE PAIGE, *Sur la génération de certaines surfaces par des faisceaux quadrilinéaires, Bul. de Belgique*, 1884, 3e *série, tome VIII*).

The locus of an S_0 for which the S_1 which unite it to four fixed S_0 meet four fixed S_2 in four S_0 of a same S_2 is a V_2^4.

2. Let there be in an S_n k S_{r_i} which we shall designate by A_i and k S_{s_i} which we shall designate by B_i, $(i = 1, \ldots k)$.

Let p be a number satisfying the $2k$ inequalities

$$r_i + p + 1 \leqq n - 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$r_i + s_i + p + 1 > n, \quad (i = 1, \ldots k) \quad . \quad . \quad (2)$$

A space S_p determines with the k spaces A_i k spaces S_{r_i+p+1}. These spaces meet the corresponding spaces B_i in k spaces $S_{r_i+s_i+p-n+1}$.

If these k spaces belong to an $S_{\sum_{i=1}^{i=n}(r_i+s_i)+k(p-n+2)-1}$,

the space S_p describes a variety $V_{(n-p)(p+1)-1}$ the order of which is to be found.

Let us suppose we have

$$\Sigma (r_i + s_i) + k(p - n + 2) = n + 1. \quad . \quad . \quad . \quad . \quad (3)$$

Let C be an S_{p+1} and D an S_{p-1} of C.

Let us designate by Δ an S_p passing through D and situated in C.

Let us take $k-1$ spaces Δ and let us number them $1, \ldots j-1, j+1, \ldots k$.

These $k-1$ spaces Δ determine with $k-1$ spaces A_i suitably chosen $k-1$ spaces S_{r_i+p+1}. These spaces meet the corresponding spaces B_i in $k-1$ spaces $S_{r_i+s_i+p-n+1}$, $(i=1, \ldots, j-1, j+1, \ldots k)$.

These spaces determine an $S_{\sum_{i=1}^{i=j-1}(r_i+s_i)+\sum_{i=j+1}^{i=n}(r_i+s_i)+(k-1)(p-n+2)-1}$

This space has in common with B_j a space

$$S_{\sum_{i=1}^{i=j-1} r_i + \sum_{i=j+1}^{i=n} r_i + \sum_{i=1}^{i=n} s_i + (k-1)(p+2) - kn - 1}$$

In its turn this space determines with A_i a space

$$S_{\sum_{i=1}^{i=j+1}(r_i+s_i)+(k-1)(p+2)-kn}$$

On account of the equality (3) the latter meets C in a single point, which determines with D a space Δ_j.

When j varies from 1 to k, one obtains k series of spaces Δ between which exists a $(1, 1, \ldots 1)$ correspondence. There are k coincidences.

The variety described by the space S_p is $V^k_{(n-p)(p+1)-1}$.

The locus of a space S_p for which the S_{r_i+p+1} which unite it to k fixed spaces S_{r_i} meet k S_{s_i} in k $S_{r_i+s_i+p-n+1}$ of a same $S_{\sum(r_i+s_i)+k(p-n+2)-1}$, $(i=1, \ldots k)$, is a variety $V^k_{(n-p)(p+1)-1}$.

The spaces A_i are evidently principal spaces of the locus of S_p, principal space having the same meaning as principal point or plane of a complex of rays.

In S_3 we find the following theorem:

The locus of an S_1 for which the S_3 which join it to four S_0 meet four S_1 in four S_0 of a same space S_3 is a variety V^4_3 (complex of order four).

3. If we regard the ordinary space as if generated by right lines we have a geometry of four dimensions. We shall now show two generalizations of the theory of GRASSMANN in this geometry.

Let us imagine k linear congruences $G_1, \ldots G_k$, and k plane pencils $(P_1, \pi_1), \ldots (P_k, \pi_k)$. Let us imagine moreover to be given a linear system C of linear complexes to the amount in number of ∞^{6-k}.

An arbitrary right line g determines k linear complexes with the

k congruences G. These have in common with the k corresponding plane pencils k lines $p_1, \ldots p_k$.

Let us now find the locus of the line g when the k lines p belong to a same complex of the system C.

Let (A, α) be any plane pencil. Let us take $k-1$ lines of this pencil and let us number them $1, \ldots i-1, i+1, \ldots k$.

Each of these lines determines with the corresponding congruence G a linear complex, which has in common with the corresponding plane pencil (P, π) a line p. The $k-1$ lines p found in this way determine a complex of the system C. This complex has a line p_i in common with the plane pencil (P_i, π_i). This line determines with G_i a complex having a line a_i in common with (A, α). When i varies from 1 to k we have k series of lines a between which exists a $(1, 1, \ldots 1)$ correspondence. There are k coincidences.

The locus of a right line for which the linear complexes that it determines with k fixed linear congruences meet k fixed plane pencils in k lines of a linear complex of a system of $6-k$ terms is a complex of degree k (order and class) to which belong the given k linear congruences.

If $k=6$, we have a theorem of GRASSMANN.

4. Let us suppose five groups of three lines $H_1, \ldots H_5$ and five nets of lines $R_1, \ldots R_5$.

An arbitrary line g determines with $H_1, \ldots H_5$ five linear congruences which meet the five corresponding nets in five lines. If these five lines belong to a selfsame linear congruence the line g describes a congruence.

Let π be a plane. Let us consider in this plane five series of lines $p_1, \ldots p_5$. Between the lines of these series it is easy to see that there is such a correspondence that to four right lines corresponds a fifth.

Let us suppose that three right lines are fixed, whilst the fourth describes a pencil. It is then easy to verify that the fifth also describes a pencil. According to an extension of the principle of ZEUTHEN there are fifteen coincidences.

The locus of a right line taken in such a way that the linear congruences which it determines with five systems of three lines have in common with five nets five lines of a same linear congruence is a congruence of the fifteenth class.

In the same way we can verify that this congruence is also of order fifteen and that it contains the generatrices of the same kind as the given lines of the five quadratic surfaces determined by these lines.

Physics. — "*Contributions to the knowledge of the ψ-surface of* VAN DER WAALS. XVI. *On the gas phase sinking in the liquid phase for binary mixtures in the case that the molecules of one component exert only a feeble attraction.*" By Prof. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. Supplement N°. 16 to the Communications from the Physical Laboratory at Leiden.

§ 1. *Introduction.* In Comm. N°. 96*b*, These Proc. Dec. 1906, p. 501 a gas phase sinking in a liquid phase[1]), the barotropic phenomenon, was treated for binary mixtures for a gas liquid plait, which crosses the ψ-surface as a transverse plait at lower temperature. Then the treatment for temperatures, at which the appearance of a longitudinal plait brings about a disturbance, was deferred to a later communication. Moreover, more special cases, as the appearance of minimum or maximum critical temperature or minimum or maximum pressure of coexistence, were left out of consideration, and the discussion was restricted to the case that retrograde condensation of the first kind occurs.

When for binary mixtures the conditions for the sinking of a gas phase in a liquid phase were treated in Comm. N°. 96*c*, These Proc. Dec. '06, p. 508 and Febr. '07 p. 660, it appeared in the first place that at least if the hypotheses mentioned there are valid, and pairs of substances are found with proper a_{22M}/a_{11M}, b_{22M}/b_{11M} and M_2/M_1 the theory of VAN DER WAALS' ψ-surface leads us to expect that barotropic plaitpoints[2]) will occur.[3]) Further that for mixtures with

---

[1]) Considerations which are not in accord either with the limited compressibility of a gas at high pressures, first stated by NATTERER in 1844, or with our present views on the mixing of two substances, induced JAMIN, C.R. 96 (1883) p. 1448, Journ. de phys. (2) 2 (1883) p. 389 to raise the question whether it should be possible that with compression of a mixture of CO_2 with air or with hydrogen, a liquid phase would collect above the gas phase. CAILLETET (JAMIN l.c.) did not succeed in realizing this.

[2]) On the peculiar phenomena which are met with in case of a barotropic plaitpoint, we hope shortly to make a communication.

[3]) That the barotropic plaitpoint found in Comm. N°. 96*c*, Dec. '06 § 5 belongs o the gas liquid plait (cf. Comm. N°. 96*c*, Febr, '07, p. 660 footnote 1) was derived rom the shape of the spinodal curve for this case, in connection with the course of the plaitpoint curve. The same thing may appear as follows: By applying the criterion (3) in Suppl. N°. 15, March '07, p. 796, we find that mixtures of a pair of substances of ratios indicated in the mentioned § belong to case (*c*), (cf. p. 276) while we may derive from VAN LAAR's fig. 22, Arch. TEYLER (2) 10 (1907) p. 138, These Proc. Sept. '06, p. 226, fig. 1, that the plaitpoint curve crosses from the side $x=0$ to the side $v=b$ (VAN LAAR's type I).

certain ratio v_{k2}/v_{k1} for not too large T_{k2}/T_{k1} (from 0 up to a certain value, see Table I loc. cit. p. 662) only one barotropic plaitpoint occurs, which in connection with Comm. N°. 96^b p. 503 and 504 pointed to the fact that for the knowledge of the course of the barotropic phenomena at lower temperature considerations in which only the transverse plait is taken into account, are not sufficient for these mixtures [1]) (see Comm. N°. 96^c p. 663).

In Comm. N°. 96^c p. 660 footnote 2 an estimation [2]) was derived about the critical temperature of helium from the observation of the barotropic phenomenon for a mixture of helium and hydrogen described in Comm. N°. 96^a These Proc. Nov. '06, p. 459. In this estimation the supposition already mentioned in Comm. N°. 96^a, p. 460, that the molecules of helium exert only an exceedingly slight mutual attraction, was found confirmed.

This suggested the investigation already announced in Comm. N°. 96^b, p. 502 on binary mixtures one of whose components is a gas the molecules of which exert no or only feeble attraction (Suppl. N°. 15, These Proc. March '07, p 786). Here a plait was described for the first time which at descending temperature appears on the

---

[1]) For mixtures of pairs of substances as meant in table I p. 662, for which $0.2'9 > T_{k_2}/T_{k_1} > 0.196$, three barotropic plaitpoints will occur one of which, however, does not belong to the absolutely stable region. At least for the larger ones of the mentioned ratios T_{k_2}/T_{k_1}, the two others belong to a plait which enters the ψ-surface from K_1, and crosses the ψ-surface as a transverse plait at lower temperature. For this the considerations of Comm. N°. 96^b will hold at least in so far as solid phases do not cause a disturbance. For the smaller ones of these ratios one of these two barotropic plaitpoints will also fall in the not absolutely stable fluid region, and so also for these we shall have to take the occurrence of three phase equilibria into account.

[2]) For the calculations in note 2, p. 660 of Comm. N°. 96^c we availed ourselves for a and b of hydrogen of the values calculated for this by KOHNSTAMM (LANDOLT-BÖRNSTEIN-MEYERHOFFER'S Physik. Chem. Tables 1905), which values had $T_k = 38.6$, $p_k = 20$ according to OLSZEWSKI, Wied. Ann. Bd. 56, p. 133, 1895 as starting point. If we derive the a and b for H_2 from $T_k = 29$ à 32, $p_k = 15$ according to DEWAR (B. A. Report 1902), the estimation for T_kHe yields about 1°, OLSZEWSKI's newer data, Ann. d. Phys. 17 (1905) p. 986: $T_k = 32.3$, $p_k = 14.2$, give it a value of more than 1° (the calculation according to note 2 l. c. yields $a_{22M}/a_{11M} = 1/50$, $T_k\text{He} = 1.3$).

This would bring about these modifications in the classification of the helium mixtures mentioned in Suppl. N°. 15, Sept. '07, § 8, that mixtures of He with H_2O, O_2, A, Ne, NO, NH_3 would belong to case (b), those with H_2, H_2S, CO_2 to case (c). For the modification which another assumption about a_{12M} (cf. p. 280) would cause in the circumstances under which the plait starting from $v = b$ occurs see Suppl. N°. 15 l. c. p. 234. A smaller a_{12M} might even again bring about a shifting in the classification in the direction from (c) towards (a).

ψ-surface from the side of the small volumes, reaches the side $x=0$ at $T=T_{k_1}$, and then passes into a plait crossing in a slanting direction from $v=b$ to $x=0$. This description was accompanied by remarks about limited miscibility in the gas state.

In Suppl. N°. 15 § 7 These Proc. March '07, p. 795 three cases were distinguished for mixtures in which one component is a gas with a feeble attraction. They are indicated as cases (a), (b) and (c) in § 9, These Proc. Sept. '07, p. 235. Case (a) corresponds with the above mentioned one; in case (b) a plait coming from $v=b$ and one coming from $x=0$ join to a single plait in a double plaitpoint [1]); in case (c) a plait starts from $x=0$, comes in contact with $v=b$

---

[1]) On the suppositions mentioned in Comm. N°. 96c p. 509 and p. 510 the data for the two double points in the net of spinodal curves, of which this double plaitpoint is one (a node) may be found in the following way (cf. Comm. Suppl. N°. 15, p. 233, note 1):

The equation for the v,x-projection of the spinodal curve on the molecular ψ-surface:

$$RTv_M^3 = 2(1-x_M)(v_M\sqrt{a_{11M}}-b_{11M}\sqrt{a_M})^2 + 2x_M(v_M\sqrt{a_{22M}}-b_{22M}\sqrt{a_M})^2 \quad (1)$$

(cf. Suppl. N°. 15, March '07, p. 788) gives as conditions for the appearance of a double point after some obvious reductions:

$$(v_M\sqrt{a_{11M}}-b_{11M}\sqrt{a_M})^2 = 2b_{11M}\sqrt{a_{11M}}.(1-x_M)(v_M\sqrt{a_{11M}}-b_{11M}\sqrt{a_M}) + \\ + 2b_{22M}\sqrt{a_{11M}}.x_M(v_M\sqrt{a_{22M}}-b_{22M}\sqrt{a_M}) \quad . \quad . \quad . \quad . \quad (2)$$

and

$$(v_M\sqrt{a_{22M}}-b_{22M}\sqrt{a_M})^2 = 2b_{11M}\sqrt{a_{22M}}.(1-x_M)(v_M\sqrt{a_{11M}}-b_{11M}\sqrt{a_M}) + \\ + 2b_{22M}\sqrt{a_{22M}}.x_M(v_M\sqrt{a_{22M}}-b_{22M}\sqrt{a_M}) \quad . \quad . \quad . \quad . \quad (3)$$

From (2) and (3) follows:

$$\frac{(v_M\sqrt{a_{11M}}-b_{11M}\sqrt{a_M})^2}{\sqrt{a_{11M}}} = \frac{(v_M\sqrt{a_{22M}}-b_{22M}\sqrt{a_M})^2}{\sqrt{a_{22M}}} \quad . \quad . \quad (4)$$

Extracting the root from this equation, we may (2) and (3) reduce to:

$$\frac{v_M\sqrt{a_{11M}}-b_{11M}\sqrt{a_M}}{\sqrt{a_{11M}}} = 2b_{11M}(1-x_M) \pm 2b_{22M}x_M\sqrt{a_{22M}/a_{11M}} \quad . \quad (5)$$

and

$$\frac{v_M\sqrt{a_{22M}}-b_{22M}\sqrt{a_M}}{\sqrt{a_{22M}}} = 2b_{22M}x_M \pm 2b_{11M}(1-x_M)\sqrt{a_{11M}/a_{22M}}. \quad (6)$$

By eliminating v_M from (5) and (6) we obtain for x_M the equation (1) of Suppl. N°. 15, March '07, p. 796 (cf. errata Proc. Sept. '07, p. 239).

The further derivation of v_M and T (see Suppl. N°. 15, March '07, p. 798) may be left to the reader (compare with these developments VAN LAAR, These Proc. May '07, p. 38 sqq. and Arch. TEYLER (2) 11 (1907) 1re partie § 5).

at lower temperature, and passes then into a plait crossing in a slanting direction [1]).

For this distinction a_{22M}/a_{11M} was always supposed so small in connection with the value of b_{22M}/b_{11M}, that the plaitpoint curve crosses from K_1 to the line $v=b$ and that three phase equilibria not yet occur at the temperatures under consideration [2]).

Now that the estimations concerning the a and b of helium justify the supposition that the plaitpoint curve [3]) crosses from $x=0$ to the

---

[1]) KUNDT, Berl. Sitzb. Oct. 1880, S. 812—824 was of opinion that it would always be possible to convert a liquid to the gas state by pressing in a gas. This view was maintained in VAN ELDIK's thesis (Leiden 1898, p. 7, cf. Comm. Phys. Lab. Leiden, Suppl. N°. 3, p. 45), where it says that the operation mentioned, if it is realized, would be the determination of the plaitpoint pressure corresponding to the temperature of observation of the pair of substances which is subjected to the experiment. There it was tacitly assumed that with sufficiently high pressure the plaitpoint state could be reached for every temperature between the critical temperatures of the components as e.g. for mixtures of methyl chloride and carbonic acid, even though it would have to be found above 750 atmospheres for hydrogen and ether, as VAN ELDIK derived taking into account the diminution which with increasing pressure is found in the decrease of the surface tension caused by one and the same increase of pressure (KUNDT loc. cit. p. 818, VAN ELDIK Thesis, p. 5, cf Suppl. N°. 3, p. 52). If we pay attention to the possibility now foreseen by the theory, that this diminution continues outside the region of observation, it seems probable in the light of the observations mentioned, that it would not be possible — here we treat as infinite, pressures which exert forces on the molecules greater than those joining the parts of them — to reduce the surface tension to 0 for the pair of substances mentioned (and the same remark applies to hydrogen and ethylalcohol) at the temperature of observation (KUNDT 21°, VAN ELDIK 9°.5), so that already at that temperature a plait crossing obliquely from $x=0$ to $v=b$ would exist on the ψ-surface.

In fact we should also derive from VAN LAAR's figure cited p. 274 footnote 3 that ether-hydrogen (and also alcohol-hydrogen) belong to VAN LAAR's type I, while according to the criteria laid down by us, they should belong to case (*c*) of this type. VAN DER WAALS' equations Contin. II p 43, however, would point out a critical temperature of complete miscibility of about $-200°$C. in the supposition of $a_{12M}=\sqrt{a_{11M}a_{22M}}$, so that according to these suppositions an obliquely crossing plait would only make its appearance below this temperature. If the existence of an obliquely crossing plait at the temperature of the above mentioned experiments should be confirmed, this might, among other things, point to the fact that a_{12M} would be considerably smaller than $\sqrt{a_{11M}a_{22M}}$ for the pair of substances mentioned (cf. p. 280).

[2]) According to this restriction case (*c*) cannot occur e.g. for b_{22M}/b_{11M} larger than a certain value (cf. Suppl. N°. 15 These Proc. March '07, p. 797).

[3]) KUENEN, These Proc. Febr. '03, p. 473 was the first to find experimentally a plaitpoint curve starting from $x=0$, and directed to the side $v=b$ for mixtures of ethane and methylalcohol.

line $v = b$ for mixtures of helium and hydrogen [1]), it is desirable to subject the barotropic phenomena for the cases mentioned to a closer examination. In this discussion for mixtures one component of which is a gas with feeble attraction, we shall again restrict ourselves and suppose that in the considered cases at the considered temperatures the second branch of the plaitpoint curve (VAN LAAR, These Proc. May '05 p. 37), starting from K_2, does not make its influence felt, so that three phase equilibria do not yet make their appearance.

§ 2. *The course of the barotropic phenomena for binary mixtures, one component of which is a gas whose molecules exert only a feeble attraction.*

In this discussion we shall have to distinguish the cases *a*, *b*, and *c* mentioned in § 1.

a. In this case a plait starting from $v = b$ and closed towards the side of the large v's, appears for $T_{km} > T > T_{k_1}$, which plait we have called gas-gasplait in Suppl. N°. 15, March '07, p. 793. If $b_{22} < b_{11}$, then θ_{pl} will be $> \frac{\pi}{2}$ for $T > T_{bpls}$ (see Comm. N°. 96^b p. 504); at $T = T_{bpls}$ a barotropic plaitpoint occurs (cf. Suppl. N°. 15 March '07 Pl. I, fig. 1); at $T < T_{bpls}$ we find a barotropic nodal line on the gas-gasplait (cf. Suppl. N°. 15, Pl. I, fig. 2). At $T = T_{k_1}$ the gas-gasplait passes into an obliquely crossing gas liquid plait. A barotropic nodal line will exist on it (see fig. 1) till it disappears under the three phase triangle, and so passes into the not absolutely stable region. As mentioned in § 1 we shall not give the description of what happens when three phase equilibria have appeared. In the same way we shall for the present disregard more complicated cases, as the appearance of two barotropic nodal lines on the gas-gasplait, three on the obliquely crossing plait etc., till further investigation may teach that these cases are possible.

If $b_{22} > b_{11}$, the plait coming from $v = b$ may reach the side $x = 0$, and pass into an oblique plait without it being necessary that a barotropic tangent chord occurs.

b. For $b_{22} < b_{11}$ a barotropic plaitpoint will occur at $T_{bpls} > T_{dpl}$ (cf. Suppl. N°. 15, March '07 p. 798). This barotropic plaitpoint, and also at $T_{bpls} > T > T_{dpl}$ the barotropic tangent chord, may

[1]) This follows also from VAN LAAR's fig. 22, Arch. TEYLER (2) 10 (1907) p. 38 with the mentioned estimations on the critical temperature and pressure of helium (cf. p. 275 note 2) and on the suppositions made (cf. These Proc. Dec. '06 p. 509 and 510).

occur both on the plait starting from $v = b$ and on that starting from $x = 0$ (figs. 2 and 3). If in the homogeneous double plaitpoint the isobar should run parallel to the x-axis, T_{bpls} would coincide with T_{dpl}. For $T < T_{dpl}$ a barotropic chord exists on the obliquely crossing plait, just as in case (a) [1]).

For $b_{22} > b_{11}$, as in this case for a, the existence of barotropic tangent chords is not required.

c. If $b_{22} < b_{11}$, a barotropic plaitpoint will make its appearance for $T_{bpls} < T_{k_1}$ and $> T_{km}$; at lower temperatures a barotropic tangent chord is found on the plait starting from $x = 0$ and closed on the side of the small v's, and at $T < T_{km}$ on the obliquely crossing plait (fig. 4). For $b_{22} > b_{11}$ as for a and b.

In fig. 5 the course of the spinodal curves (continuous) and of the connodal curves (lines consisting of dashes) on the ψ-surface for the unity of weight has been more fully represented for a case c. The figure has been construed with a view to mixtures of helium and hydrogen. In this we adopted the hypotheses mentioned in Comm. N°. 96^c, Dec. '06, p. 509 and 510, and put for hydrogen $T_{k_1} = 32{,}3$, $p_{k_1} = 14.2$, for helium $T_{k_2} = 1{,}3$, $b_{\text{MIIe}} = \frac{1}{2} b_{\text{MII}_2}$ (p. 275 note 2) [2]). The volume v is expressed in the theoretical normal volume of a molecular quantity as unity. The point K_m has been calculated according to VAN DER WAALS Cont. II, p. 43. The spinodal curves have been constructed as in Suppl. N°. 15, March '07, p. 788. P_b is the barotropic plaitpoint, calculated in the way indicated in Comm. N°. 96^c, Dec. '06, p. 510. Further the plaitpoint curve $K_1 K_m$ calculated according to the equation given by VAN LAAR,

---

[1]) In the light of our present knowledge of the behaviour of mixtures and divested of the considerations which are incompatible with it (cf. p. 274 footnote 1) the phenomenon deemed possible by JAMIN, C. R. 96 (1883) p. 1451, Journ. phys. (2) 2 (1883) p. 383, would be described as follows: On compression of a gas above a suitable quantity of liquid (see p. 281 note 2), this liquid is made to dissolve at first under plaitpoint circumstances after which on further pressing in of the gas into the thus formed homogeneous phase a phase richer in the least volatile component (called by JAMIN liquid, by us in certain cases, cf. Suppl. No. 15, March '07, § 4, second gas phase) may separate *above* the phase which is richer in the most volatile component. If this phenomenon could be realized, we should have to deal with a case b for a temperature $T > T_{dpl}$, and in which the line RQ (see fig. 6) intersects the plait starting from $v = b$ in such a way that for the intersected connodal tangent chords $\theta > \frac{\pi}{2}$.

[2]) However, on account of the uncertainty which still prevails about $T_{k\text{He}}$ and $p_{k\text{He}}$, and in view of the probability that $a_{12M} < \sqrt{a_{11M}\, a_{22M}}$ (see p. 280) it is still to be considered as quite possible that He—H_2 belongs to case (b), as was supposed in Suppl. N°. 15.

These Proc. April '05 p. 652 has been included in the diagram. The second branch of the plaitpoint curve is not to be distinguished from the straight line HK_2 on the scale on which the diagram has been drawn.

For the connodal curves the points of intersection with the line $x = 0$ representing the points of saturation for pure hydrogen have been calculated. For this purpose the constants of saturation have been used, which have been calculated by DALTON [1]) for a substance that follows the equation of state of VAN DER WAALS with constant a and b. For the rest the course of the connodal curves for which for $T \geqq T_{km}$ also the plaitpoints are known, has been represented schematically. This applies particularly to the points of intersection of the connodal curve for $T = 20$ with the line $v = b$, so that also the course of the connodal curve, particularly of the gas branch, is uncertain in the neighbourhood of the line $v = b$. The line CD represents the experimentally determined barotropic tangent chord for $T = 20$ (see Comms. N°. 96^a and N°. 96^c Febr. '07 p. 660 footnote 2).

The situation of the line CD with respect to the connodal curves might point to T_{km} being higher than was calculated by us, which may be due either to the critical temperature of helium being lower than was assumed by us here, or to a_{12M} being $< \sqrt{a_{11M} a_{22M}}$ for mixtures of He—H_2 [2]).

The course of the barotropic plaitpoints and barotropic tangent chords in case (c), and also in case (b), if they occur on the plait starting from $x = 0$, corresponds for the higher temperatures with that for the case that the branch of the plaitpoint curve starting from K_1 crosses the ψ-surface from $x = 0$ to $x = 1$, for which case the course was described in Comm. N°. 96^b. For the lower temperatures we meet with this difference that in the cases considered in this comm. the barotropic tangent chord continues to exist on the plait, till it disappears under the three phase triangle, whereas in the cases considered in Comm. N°. 96^b the barotropic tangent chord may also vanish from the plait through a barotropic plaitpoint (lower barotropic plaitpoint temperature, see Comm. N°. 96^b p. 504). The latter must even be the case if for $T \geqq T_{k_2}$ no three phase equilibria appear as yet (cf. p. 275 note 1).

---

[1]) J. P. DALTON, Phil. Mag. April 1907, p. 520.

[2]) The same remark concerning a_{12M} for mixtures of H_2 with other substances might be derived as follows: for $CO_2 - H_2$ (the same holds for CO_2—O_2) from a comparison of the experimentally determined portion of the plaitpoint curve with that calculated in the same way as above for He—H_2; for H_2 — ether and H_2 — alcohol see § 1 p. 277 note 1).

VAN DER WAALS, These Proc. Jan. '07 p. 528 calls attention to the influence of $b_{22}\ b_{11}$ on the occurrence of barotropic phenomena by stating this rule: "When the most volatile substance has the greatest limiting density, the gas phase can be specifically heavier than the liquid phase." In connection with what was discussed above we may now supplement this rule as follows: If of a binary mixture the more volatile component has the greater limiting density, the gas phase will be made to sink in the liquid phase by compression with suitable concentration and temperature, provided the more volatile component has so feeble an attraction that pressing in of this latter component cannot make the liquid phase of the less volatile component dissolve in the gas phase at definite [1]) temperatures even at the highest (comp. p. 277 note 1) pressures. [2]) It is implied in the terms of this rule that it has been supposed that no two liquid phases occur.

It is not excluded that also in other cases sinking of the gas phase in the liquid phase might occur. [3])

If we apply this rule to pairs of substances of which data are available for a_{22M}, a_{11M} and b_{22M}, b_{11M}, it appears that only for $He—H_2$ it may be expected on reasonable grounds [4]) that barotropic phenomena occur at not too high pressures [5]). Further investigations will have to reveal whether for mixtures of pairs of substances as nitrogen

---

[1]) Also at higher temperatures than these barotropic phenomena may then occur.

[2]) In the case of compression of a gas above a liquid, starting from the pure substance in the way as was done in KUNDT's experiments we describe on the ψ-surface a curve the v, x-projection of which is a straight line joining a point of the line $x = 0$ with the point $v = 0$, $x = 1$. For the liquid phase to disappear at a definite, suitable temperature just under plaitpoint circumstances, we must start from a definite quantity of liquid so that the volume is represented by SQ (see fig. 6). If the quantity of liquid from which we start, is smaller, the liquid phase will evaporate (be dissolved in the gas phase), if it is larger the gas is dissolved in the liquid phase (cf. VAN DER WAALS, Cont. II, p 136). Only if the diffusion is not rapid enough to ensure equilibrium all through the tube, solution of the liquid under plaitpoint phenomena may be observed also with other quantities of liquid as corresponding with v_Q, as has been set forth by KUENEN's experiments on the influence of phenomena of retardation.

[3]) See e.g. § 1, p 275, note 1.

[4]) Though for mixtures of e.g. helium and acetonitril the available data with application of the special hypotheses assumed in this § (concerning the equation of state etc.) would point to the fact that at high pressures barotropic phenomena might still just occur, it is impossible to express a definite expectation with regard to this on account of the influence of the uncertainties, both in the data and in the validity of the mentioned suppositions.

[5]) This was mentioned in Comm. No. 96*b* Dec. '06 p. 504.

and a light oil with high critical temperature [1]), nitrogen-lithium, argon-kalium, mercury-iron etc. sinking of the gas phase in the liquid phase could be realized.

§ 3. *On the conditions for the occurrence of barotropic phenomena.* It appeared in § 2 that with a suitable ratio of the limiting densities the occurrence of the barotropic phenomena depends to a great extent on the ratio of the attractions of the molecules of the two components, hence on the ratio of the critical temperatures. The same thing may also be derived in the following way, more independent of the particular hypotheses which have led to the consideration of obliquely crossing plaits.

To bring about the phenomenon of the gas phase sinking in the liquid phase, the gas phase will have to be much more compressible than the liquid phase, and even on compression the gas phase must not dissolve in the liquid phase. For this the temperature will have to be pretty far below the critical temperature of the least volatile component (T_{k_1}), but still far above that of the second component (T_{k_2}). This points to a large difference between the critical temperatures of the components.

If for the pair of substances considered retrograde condensation of the first kind occurs, the coexisting phases indicated by the points L and G on the ψ-surface for the molecular quantity (see fig. 7) [2]), can only have the same density if $M_2 > M_1$.

Only when on the plait on the molecular ψ-surface connodal tangent chords appear for which the angle with the axis $x = 0$: $\theta > \frac{\pi}{2}$, the coexisting phases can have equal density for $M_2 < M_1$.

As the difference between x_g and x_l is larger, and so the connodal tangent chords deflect more rapidly from the side $x = 0$, a smaller difference between M_2 and M_1 will suffice to establish equal densities in G and L.

This will be the more the case the more the plait extends towards the side $v = b$.

The latter is particularly furthered by a small ratio a_{22M}/a_{11M} (cf. Comm. Suppl. N°. 15 Pl. I fig. 1 and Pl. II), so by a small ratio of the critical temperatures, b_{22M} smaller than b_{11M} also tending in this direction.

---

[1]) Mr. F. M. Gilley of Boston drew our attention to mixtures of air and oil.

[2]) The dotted lines indicate that the considerations of this § hold both for the case that at lower temperature the plait crosses the ψ-surface as a transverse plait, and for the case that it extends towards $v = b$.

H. KAMERLINGH ONNES and W. H. KEESOM. "Contributions to the knowledge of the ψ-surface of VAN DER WAALS. XVI. On the gasphase sinking in the liquid phase for binary mixtures in the case that the molecules of one component exert only a feeble attraction."

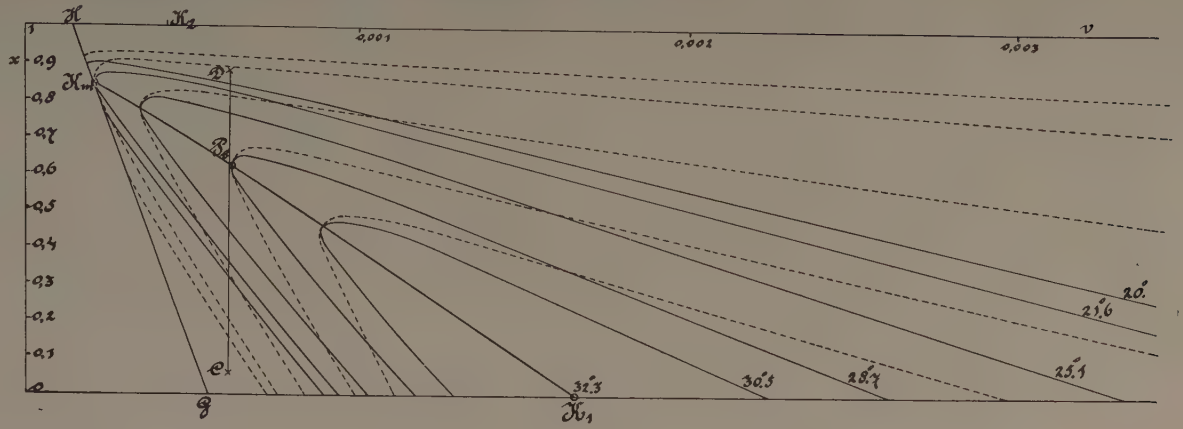


Fig. 5.

Fig 1.

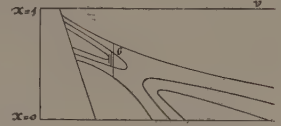


Fig. 2.

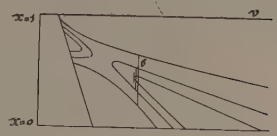


Fig. 3.

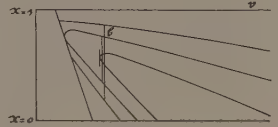


Fig. 4.

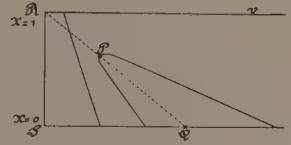


Fig. 6.

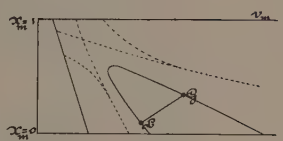


Fig. 7.

Hence we get as conditions for the possibility of the occurrence of barotropic phenomena:

The second component must have: T_{k_2} small compared with T_{k_1}, and by preference also: $M_2 > M_1$ and $b_{22M} < b_{11M}$.

This becomes still clearer by the application of equations (2) and (4) of Comm. N°. 79, April '02, p. 659:

$$x_l = x_g\, e^{\frac{\varphi'_g - \varphi'_l}{MRT}}$$

$$\frac{\varphi'_g - \varphi'_l}{MRT} = \left\{ \alpha \frac{T}{p_m} \frac{dp_m}{dT} - \beta \right\} \frac{p_m (v_g - v_l)}{MRT}$$

which determine the ratio of the concentrations of gas and liquid phases of a binary mixture in which the quantity of one component is small, if the law of the corresponding states may be applied. The connodal tangent chord will rapidly deflect from the side $x = 0$, if the exponent of e assumes a considerable negative value. The greatest influence on this exerts $\alpha = \frac{1}{T_{k_1}} \left(\frac{dT_{xk}}{dx} \right)_{x=0}$, on account of the value of the coefficient $\frac{T}{p_m} \frac{dp_m}{dT}$ (> 7); so T_{k_2} will have to be small with respect to T_{k_1}. The influence of $\beta = \alpha - \gamma$, if $\gamma = \frac{1}{v_{k_1}} \frac{dv_{xk}}{dx}$ (cf. Comm. N°. 81, Oct. '02 p. 325) is only of secondary importance. To tend at least in the right direction, γ would have to be negative, so $b_{22M} < b_{11M}$ [1]).

Physiology. — *"An investigation of* Mr. J. W. A. Gewin, *on the relation of pepsin to chymosin."* By Prof. C. A. Pekelharing.

That gastric juice possesses the power, on the one hand to digest proteins under acid reaction, on the other hand, to curdle milk under neutral or scarcely acid reaction, is generally attributed to the presence of two different enzymes in the gastric juice, viz. pepsin and chymosin. This opinion is chiefly based upon an observation of Hammarsten, who was the first to throw light on the changes that take place in milk when it is coagulated by means of rennet. Hammarsten found that an extract from the mucous membrane of the stomach, which, when prepared fresh, could digest proteins as well

[1]) The more elaborate mathematical treatment of the conditions for the occurrence of barotropic phenomena, as sequel to Comm. N°. 96*c*, will be postponed till further experiments call for a further discussion.

as curdle milk, after having been digested for a few days with hydrochloric acid at a temperature of 37° C., no longer showed the action of rennet, but had preserved its peptic action. From this it could not but follow that each of these actions depended upon a separate agent.

Meantime doubts have gradually arisen as to the correctness of this opinion. That there must at any rate be a very close connection between the proteolytic action of pepsin and the enzym of rennet, was made probable by the experience that all enzym-solutions with a proteolytic action, no matter whether they are of animal or of vegetable origin, can also act like rennet. And, as I communicated some years ago in this Academy, and as was afterwards corroborated by NENCKI and SIEBER, it could also be proved that all kinds of preparations of pepsin, also when a long digestion with hydrochloric acid and a purification as careful as possible had preceded, are able to act like rennet.

In 1904 there appeared an investigation by PAWLOW and PARASTSCHUK [1]), in which they demonstrated that pepsin and chymosin must be considered as the same substance. These investigators found that in different liquids containing enzym not only the proteolytic and the curdling power are always found side by side, but that also a proportionately greater curdling power corresponds to a greater proteolytic action. That this is not found in some enzym-solutions of commerce appeared to be owing to the presence of other substances; as soon as their effect was destroyed, the proportionality came to light. A solution of rennet, according to HAMMARSTEN prepared by means of carbonate of magnesia from gastric juice, which, in his opinion, no longer contained any pepsin at all, appeared to be a very good digester of albumen, if only the noxious influence of magnesia-salts was taken away. No more was it proved by HAMMARSTEN, — as PAWLOW explained — that a pepsin-solution can be freed from rennet by digestion with hydrochloric acid, as the proteolytic action had been examined, while the liquid still had an acid reaction; the curdling action, on the other hand, after neutralization, by which the enzym might be easily destroged.

Against PAWLOW's explanation objections have been raised. Especially two Swedish investigators, BANG [2]) and SCHMIDT-NIELSEN [3]), have defended HAMMARSTEN's point of view. The investigation of Mr. GEWIN

---

[1]) Zeitschr. f Physiol. Chemie, Bd. XLII, S. 415.
[2]) Zeitschr. f. Physiol Chemie, Bd. XLIII, S. 358.
[3]) Ibid. Bd. XLVIII, S. 92.
[4]) PFLÜGER's Archiv. Bd. LXXIX, S. 425.

refers principally to the grounds alleged by these two authors for the duality-hypothesis.

In the first place he has occupied himself with an inquiry into the correctness of the conclusion previously drawn by BANG [4]) from a number of experiments, that there is not only a difference between pepsin and rennet, but also that even the enzym of rennet does not possess the same qualities in different kinds of animals. BANG continued to apply the old name, chymosin, to the enzym of rennet, as it is found in the calf. From this he distinguished by the name of parachymosin the enzym that can be got from the mucous membrane of the pig-stomach. The difference showed itself in the fact that parachymosin, when diluted, became sooner inactive than chymosin, that it showed a greater activity by the addition of chlorcalcium, was more proof against heating to 70° C. and less so against the action of alkali.

With reference to extracts from the mucous membrane of the stomach of calf or pig GEWIN could corroborate these differences; only he did not find the difference in the promotion of the activity by adding chlorcalcium as important as BANG. However, it was a different thing, if not the extracts themselves were examined but the enzym extracted therefrom by dialysis, and purified as much as possible in the way formerly communicated by me. The better the purification had taken place, the smaller the difference became. The extract from the mucous membrane of the calf-stomach loses its power to curdle milk when, neutralized, it is heated for 10 minutes to 70° C.; however, its power is but little reduced, if it is mixed with caustic soda to 0.01 % and neutralized again after half an hour. With the extract of the mucous membrane of a pig-stomach it is just the reverse. With the enzym of the calf, purified as much as possible, the resistance against heating appeared to have become great, against alkali small. From this it must therefore be deduced that the difference does not lie in the enzym itself, but that it is caused by other substances occurring in the extract. Indeed, it could be proved experimentally that the extract from the membrane of the calf-stomach contains substances which protect the enzym against the action of alkali, but make it the more sensitive to heat. Of a solution of purified pig-enzym (which possesses the qualities of BANG's parachymosin) one half was diluted with water, the other with an extract from the mucous membrane of a calf-stomach, which extract had been deprived of all enzym by heating it for one hour to 80° C. and then neutralized. Of both solutions 2 cc. mixed with 8 cc. of milk caused curdling in 30 sec. A part of each was heated for

10 minutes to 70° C., another part for half an hour left in contact with 0.01 % Na HO and then neutralized again. Now the result was:

	After heating	After action of alkali
2 cc. enzym with water + 8 cc. milk	curdling in $2^1/_2$ min.	no curdling
2 „ „ „ extract + 8 „ „	no curdling	curdling in 11 min.

Gewin also examined two rennet-preparations of commerce, one Dutch of van Hasselt and one Danish of Hansen. Both showed the qualities of Bang's chymosin. But when, by dialysis and precipitation with acetic acid, the enzym had been isolated and at least for the greater part been freed from impurities, they had become much more susceptible to alkali and much less so to heating.

That the enzym is destroyed not only by alkaline, but gradually also by neutral reaction has been made clear by Pawlow and corroborated by Gewin in numerous experiments. From this Gewin explains the difference found by Bang between chymosin and parachymosin, the solution being diluted. What Bang calls chymosin is the enzym mixed with substances protecting it from alkali. When those substances are present, it may be assumed that the enzym is better proof against the dilution with water, by which the number of hydroxyl- and metal-ions increases. A solution of purified enzym (parachymosin), possessing the same curdling power as a not purified solution of calf-enzym (chymosin), shows, when diluted, sooner a decrease in action, and consequently must, also sooner, show the promoting influence of the addition of chlorcalcium.

So there is no reason for assuming different rennet-enzymes in different kinds of animals. The difference does not lie in the enzym but in other substances originating from the mucous membrane of the stomach. If it is necessary to give a separate name to the enzym of the gastric juice that can curdle milk, it is sufficient to use the word chymosin for it.

But is even this necessary? Should it be assumed that chymosin is different from pepsin?

To the solution of this question Gewin has devoted the second part of his investigation. It was tried in vain to divide the enzym into a proteolytic and a curdling part. It is a well-known fact that proteins, undissolved and at a temperature of 15° C. put into a pepsin-solution, take up and keep back this enzym, so that it is not to be separated from it by washing it out. Coagulated and minced hen's albumen was put in a solution of purified pepsin in 0.2 % HCl. Now, if chymosin were a different matter from pepsin, only the last mentioned would perhaps be extracted from the solution by the albumen. It appeared, however, that the liquid filtered from the

albumen after some hours, had lost not only the peptic but also the curdling power. Indeed, the same negative result had already been arrived at by JACOBY, who for these experiments did not use hen's albumen but caseine [1]).

In the second place it was examined whether a separation into two enzymes could be brought about by dialysis. When pepsin, dissolved in hydrochloric acid, is dialyzed against distilled water, it is partly precipitated, most completely at a low temperature, as soon as the quantity of acid has gone down to about 0.02% HCl. Always, however, a considerable part remains dissolved, which, with the aid of ammonium-sulfate — if the solution does not contain much albumose through 50% saturation with this salt — can be precipitated. If pepsin and chymosin are different matters, it cannot be deemed improbable that they also differ in solubility, that therefore the precipitate in the dialyser should contain more of either one or the other matter than the liquid filtered from it. Also in this way, however, a separation into two enzymes, did not succeed.

SCHMIDT—NIELSEN, however, has communicated experiments from which it appears that, though not a complete, still a partial separation of pepsin and chymosin is possible. A strongly active extract from the mucous membrane of the calf-stomach, prepared with hydrochloric acid, was divided into two parts. One was preserved at a low temperature, the other at 37° C. After some days the heated part had for the greater part lost its power to curdle milk, under a neutral reaction; at acid reaction, however, protein was still strongly digested. Now both liquids were neutralized and the one not heated so much diluted that the curdling power had become as weak as that of the one heated. After that the two liquids were rendered equally acid with hydrochloric acid and digested with fibrine. The fibrine was much quicker dissolved by the heated liquid than by the diluted one, not heated. During the process of heating, therefore, the chymosin had been chiefly lost, the pepsin however not.

This experiment would certainly be convincing, if the neutralization had the same effect on the heated liquid as on the one not heated. This, however, is not the case. The extract contains substances protecting the enzym from the action of alkali; also when no more of this is added than what is necessary to attain a neutral reaction. If the extract is preserved at a low temperature, these substances remain for a long time undisturbed, but if the acid extract is heated to 37° C., they are destroyed. GEWIN has proved this by ample experiments, of which a detailed account is given elsewhere. At the

[1]) Biochem. Zeitschr. Bd. I, S. 66.

outset the enzym in the extract of rennet is quite proof against neutralizing, but after having been digested for a few days at 37° C. this power of resistance becomes smaller, and then diminishes quickly. Now, if the neutralized liquid, in order to determine the curdling power, is mixed with milk, the reaction remains neutral and no curdling arises. However, if it is rendered acid again, soon after the neutralisation, a sufficient quantity of enzym is left to digest protein. Also if the not heated solution of the enzym, before being neutralized, is sufficiently diluted with 0.2% HCl, neutralisation herein causes a rapid decrease and at last an annihilating of the curdling power. Thus the curdling time of such a solution was, 8 times diluted, 10 seconds, directly after the neutralisation $2^1/_2$ to 4 minutes, whilst the milk, mixed in the same proportion with the solution half an hour after the neutralisation, was not yet curdled after 20 minutes.

In all experiments, on the other hand, at which the noxious action of alkali was avoided, the curdling and proteolytic power of the enzym solutions appeared to keep pace with each other.

Summing up the result is therefore that not a single reason is left to assume a difference between pepsin and chymosin.

No more is there any reason to stick to the opinion of NENCKI and SIEBER, which I formerly shared, according to which pepsin should be considered as a molecule, which, through different groups of atoms, on the one hand should have a proteolytic, on the other hand a curdling action. The basis for such an idea, the opinion that the activity in one direction could be preserved, whilst that in the other direction was lost, I must now consider as having lost its foundation. The opinion defended by SAWJALOFF, is far more acceptable, who considers the alteration of caseine, of which the formation of cheese is the consequence, as the beginning of digestion, of proteolysis [2]). This opinion has, I believe, become more probable by the experiments made of late about the alterations caseine undergoes under the influence of rennet, particularly by the investigation made some time ago in my laboratory by Miss VAN HERWERDEN [1]). From these it has appeared that caseine, at a very weak acid or neutral reaction and at a temperature not much lower than 37° C. in a solution of rennet — either a preparation of commerce or pepsin purified as well as possible — soon falls asunder into paracaseine, which when it does not directly become insoluble as a lime-compound, cheese, continues to change, and other substances, among which

[1]) Zeitschr. f. Physiol. Chem. Bd. XLVI, S. 307.

[2]) Ibid, Bd. LII, S. 184.

a protein, provisionally called substance C by Miss VAN HERWERDEN. Not until the enzym has been able for a long time to influence these substances, does it form primary albumose from them. At the same time, however, the enzym also appeared at neutral reaction to form from coagulated albumen primary albumose, though in a small quantity. So there is every reason to consider curdling of milk as a proof of the first stage of proteolysis.

Taking this into consideration, it is not so wonderful, as it has been regarded, that all kinds of proteolytic enzymes possess the power of curdling milk, though in natural circumstances they never come in contact with caseine. For then the peculiarity is not to be sought for in the enzyme, but in the caseine, the splitting of which already can be observed in a stage of the digestion, in which with other proteins alteration is still quite imperceptible.

Physics. — "*The intensities of the components of spectral lines divided by magnetism*". By Prof. P. ZEEMAN.

If a spectral line is resolved into a triplet by the application of a magnetic field, the two outer components and the middle line will generally differ in intensity. According to the elementary theory of LORENTZ of the phenomenon of magnetic resolution there exists a simple relation between these intensities.

Let I_1 and I_3 be the intensities of the outer components and I_2 that of the middle line then we may expect that

$$I_1 = I_3 = \tfrac{1}{2} I_2 \quad , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It has been often asserted, that generally this relation is not fulfilled, and that triplets frequently have in contradiction with (1) a weak middle line and strong outer components.

Really some cases [1]) can be cited, in which the intensities differ from what may be inferred from equation (1). In numerous cases however this contradiction is only apparent, no attention having been paid to a circumstance presently to be mentioned and not yet examined in connexion with our present subject.

In the very important investigation by RUNGE and PASCHEN [2]) a calcspar prism was placed before the tube placed in the magnetic field. By means of a quartz lens the two images given by the calc-

[1]) The lines exhibiting the partial polarization observed by EGOROFF and GEORGIEWSKY (C.R. **124**, **125**. 1897) are meant here.

[2]) C. RUNGE u. F. PASCHEN Abh. der Berl. Akad. Anhang. 1902.

spar are projected in the plane of the slit of the spectroscope. The two images could be examined separately.

"Bei richtiger Stellung des Kalkspaths bestand das eine Bild aus Licht, dessen elektrische Schwingungen in der Lichtquelle parallel den Kraftlinien vor sich gehen, das andere Bild aus Licht, dessen elektrische Schwingungen in der Lichtquelle auf den Kraftlinien senkrecht stehen. Dass die Ebene der Schwingungen nach dem Durchsetzen des Kalkspaths durch die Quarzlinse gedreht wird, thut nichts zur Sache".

Bij means of this arrangement the components with vertical vibrations are undoubtedly separated from those with horizontal ones. The main object of RUNGE and PASCHEN's investigation being the connexion between series and magnetic separation there is no objection to be made. The case is changed however as soon as the relative intensities of the components in the emitted light are under investigation, for these under certain circumstances could be essentially altered. If vertical and horizontal vibrations are reflected differently by the grating, the rotation of the direction of vibration in the beams passing through the quartz lens of course will be apparent in the observed intensity.

Polarizing effects of gratings are well known and generally the direction of vibrations relatively to the grooves must be of importance.

I had not anticipated that this circumstance would give rise to such striking effects as were observed by me in some experiments with a large ROWLAND grating. I have only made some observations with the yellow mercury lines, observing in the spectrum of the first order. The incident rays made an angle of about 19° with the normal to the grating, and in this latter direction observations were made or photographs taken. A vacuum tube charged with some mercury [1]) was placed in the magnetic field and by means of a glass lens an image was projected on the slit of the spectroscope. The light emitted at right angles to the horizontal magnetic lines of force was investigated.

In figure 1. a reproduction is given of the triplet in which the line 5769.4 is resolved. The distribution of intensities is in absolute contradiction with equation (1).

Observations with a calcspar and a sodium flame, the light of which was incident on the grating at about the same angle as above specified, the direction of observation being normal to the grating, showed at once that the light reflected from the grating

[1]) F. PASCHEN, Physik. Zeitschr. Jahrg. 1 p. 478. 1900.

was strongly polarized. The vertical vibrations were strongly preponderating.

The influence of a rotation of the plane of polarisation of the yellow mercury light on the distribution of intensities in the triplet was then examined. The plane of polarization was rotated by means of quartz plates with faces perpendicular to the axis placed in front of the slit. I had at my disposal two small plates of 2.15 resp 4.17 mm. thick. According to GUMLICH [1]) the rotation for mercury light of wavelength 5769 in a quartz plate 1 mm. thick, is at $t = 20°$ 22°.718 and hence the rotation in my plates amounted to

$$22.72 \times 2.15 = 48°.90 \text{ en } 22.72 \times 4.17 = 94°.7.$$

The change in the distribution of light is at once apparent. In figure 3 the outer components are hardly visible. The negative reproduced corresponds to the case in which the plate rotating the plane of polarization 94°.7 is in front of the slit.

Figure 2 corresponds to the case in which the incident vibrations are inclined at about 45° to the slit. It may be remarked that in this case the real distribution of intensities between the components, as existing in the emitted light, is observed.

Vertical and horizontal vibrations now being equally present in each of the components, and hence the circumstances as to vibrations being the same for the three components, the polarization by the grating is eliminated.

The distribution of light in figure 2 is certainly not in contradiction with equation (1) and eye observation seems to confirm it numerically also. Of course a photographic reproduction is not sufficient for a comparison of intensities and a numerical test must be reserved for a future paper.

For an estimation of the real ratio of intensities of the components of a divided spectral line henceforth care must be taken that for the region of the spectrum under review the vibrations in the incident light are inclined at an angle of 45° C. to the slit.

If in the case of a complicated division of a spectral line some components are weak, it will sometimes be possible to strengthen these components by placing a quartz plate of suitable thickness in front of the slit. This will be feasible in all cases in which the incident vibrations are not those most favoured by the grating.

Of course also with other spectroscopes this device does apply

[1]) GUMLICH. Wied. Ann. Bd. **64** p. 333. 1898.

e. g. in the case of a MICHELSON echelon spectroscope, if the incident light has been previously analyzed by means of an auxiliary spectroscope. Reflection and refraction in the glass prisms of course weakens to different amounts vertical and horizontal vibrations.

Cases in which relation (1) fails are to be observed in some spectra with many lines (e. g. iron). Among adjacent magnetic triplets some are to be detected in which the distribution of intensity in one resembles figure 1, in the other figure 2. Without further analysis one may conclude that for the one or for the other relation (1) fails.

EXPLANATION OF THE PLATE.

The figures are thirtyfold enlargements of negatives concerning the mercury line 5769, 4.

In all cases the image of the source was projected on the slit with a glass lens.

Fig. 1. No quartz plate in front of slit.

Fig. 2. Quartz plate, rotating plane of polarization 45° in front of slit. The distribution of light corresponds to that in source.

Fig. 3. Quartz plate, rotating plane of polarization 90° in front of slit. Though the time of exposition was thrice that used with the other figures, there appear only traces of the outer components in the original negatives.

Chemistry. — "*On lupeol.*" By Prof. P. VAN ROMBURGH.

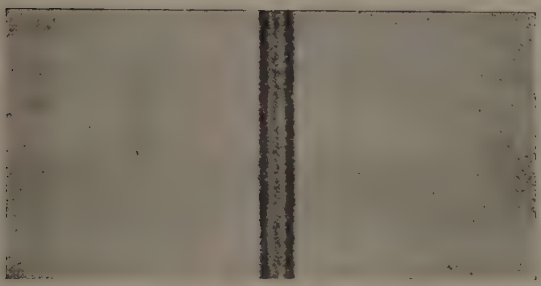
In the Comptes rendus of June 24, 1907, JUNGFLEISCH and LEROUX state that lupeol cinnamate occurs in the gutta percha of *Palaquium Treubii* BRCK.

I have demonstrated previously that cinnamic acid may be obtained from this species of gutta, whereas lupeol cinnamate proved to be a constituent of different commercial varieties of gutta percha [1]).

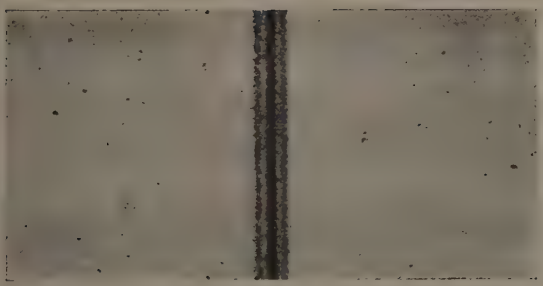
JUNGFLEISCH and LEROUX have now studied the lupeol obtained by them and state that this substance on heating suddenly on the "bloc Maquenne" melts at 190°—192°, then immediately solidifies and melts again at 212°. They explain this phenomenon by assuming that lupeol loses water and is converted into a hydrocarbon, melting at 212°, to which they give the name of lupeylene. At 130° lupeol would lose water slowly, very rapidly so at 150°—160° and suddenly at 190°.

[1]) B.B. **37** (1904) 3442.

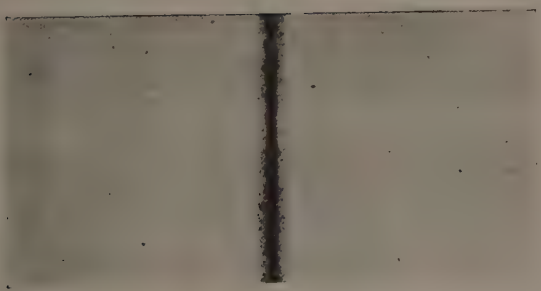
[2]) Diss. Utrecht 1906.



1. No quartz plate in front of slit.



2. Quartz plate, rotating plane of polarization 45° in front of slit.
Intensities as in source.



3. Quartz plate, rotating plane of polarization 90° in front of slit.

On treating lupeol with acetic anhydride and sodium acetate at 170°, they did not obtain lupeol acetate, but lupeylene, and they argue that the acetate cannot be obtained by the ordinary methods owing to the lupeol losing water so readily.

But some time ago (loc. cit.) I obtained with Dr. v. D. LINDEN an acetate, by acetylating lupeol; whilst Dr. COHEN also prepared this ester and studied several of its reactions.

It, therefore, did not seem to me superfluous to repeat the experiments of these French chemists, and to again prepare and analyse the lupeol acetate, so as to make sure that this substance really exists; and that Dr. COHEN, who did not analyse it, because the properties coincided with those of my preparation, and because a mixture of his acetate with lupeol exhibited a considerable lowering of the melting point, was really in possession of the substance.

In order to observe readily an eventual separation of water, and to see and weigh the same, I, first of all, heated lupeol for many hours in one of the limbs of a reverted U vacuum tube placed in an oilbath at 190°, whilst the other limb was cooled in a Weinhold's glass containing liquefied ammonia. In the limb containing the lupeol a sublimate of beautiful crystals had deposited above the oil surface whilst a slight deposit had also formed in the cooled limb.

The weight of the lupeol was 0.5403 gram.

The deposit in the cooled limb weighed 0.0065 gram.

On heating the same at 100° there remained 0.0046 gram.

Therefore only traces of water could have been present in the cooled limb.

The sublimate in the heated limb melted at 212°—213°.

In another experiment, 1.0806 gram of lupeol was weighed in a glass boat and placed in a horizontal tube which could be heated in an airbath. The tube was connected to a reservoir with sulphuric acid and the whole apparatus was evacuated by means of a water-airpump. First I heated the apparatus for ten hours at 140°—160°; the loss of weight amounted only to 0.0066 gram, but it must be observed, however, that a sublimate had formed in the tube just above the boat. Then the substance was heated in the same manner for six hours at 190°—200°. The total loss in weight then amounted to 0.041 gram, but as the sublimate weighed 0.039 gram it was in reality only 0.002 gram. A separation of water, which would have amounted to 0.040 gram, was therefore again out of the question.

The residue of the two experiments, after being recrystallised from

acetone, was combusted with lead chromate and the result showed that the lupeol had remained unaltered.

0.1991 gram yielded 0.2147 gram H_2O and 0.6172 gram CO_2

	H.	C.	
Found :	12.08	84.54	
Calculated :	11.49	84.85	(for $C_{31} H_{50} O$)[1]).

On boiling with acetic anhydride (10 parts) and sodium acetate (1 part), the residue could be converted readily into an acetate melting at 213° as shown by the analysis :

0.2191 gram yielded 0.2251 gram H_2O and 0.6588 gram CO_2

	H.	C.	
Found :	11.51	82.04	
Calculated :	10.93	82.41	(for $C_{33} H_{52} O_2$).

For the purpose of comparison the acetate of non-heated lupeol was prepared and analysed in the same manner. It melted at 212°.

0.2113 gram yielded 0.2169 gram H_2O and 0.6362 gram CO_2

	H.	C.
Found :	11.5	82.11
Calculated :	10.93	82.41

A mixture of the two acetates analysed also melted at 212°, whilst the acetate mixed with lupeol gave a strong depression of the melting point.

In another experiment, lupeol was heated at 200° for $2^1/_2$ hours in a current of dry carbon dioxide. A small calcium chloride-tube attached showed a slight increase of weight, but it appeared that a little solid matter had again volatilised with the current. The heating was then continued for six hours and the residue heated finally until the mass began to melt. On treating the same with benzoyl chloride and pyridine it was easy to obtain the lupeol benzoate, (m.p. 264°) proving that the lupeol has not passed into the hydrocarbon.

Finally I have also heated lupeol with acetic anhydride and sodium acetate in a sealed tube for three hours at 170°. The reaction product after being treated with water was recrystallised from a mixture of acetone and alcohol. The melting point of the product obtained was

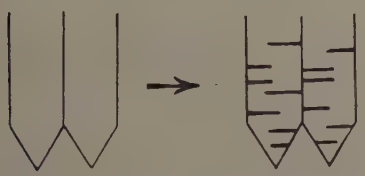
[1]) I will not go into the question whether it would be better to assign to lupeol the formula $C_{30} H_{50} O$.

212°. An addition of lupeol acetate from a previous preparation did not affect the melting point. If, however, it was mixed with lupeol or with lupeol which had been heated for some time at 190° a serious depression (about 20°) of the melting point could be observed.

The experiments described, therefore, prove convincingly that lupeol (obtained from bresk) is not converted into lupeylene under the circumstances mentioned by JUNGFLEISCH and LEROUX.

As lupeol might perhaps exist in two modifications, Dr. F. M. JAEGER, to whom I wish to convey my best thanks, was kind enough to study the behaviour of lupeol on melting. Dr. JAEGER communicates to the following particulars me:

"If lupeol is melted to a singly-refracting liquid L, which takes place very sharply, the mass, on cooling, solidifies partly to an aggregate of broad pointed needles A, glittering in high interference colours, partly to a horny singly-refracting mass A', which frequently exhibits globular spherolites, resembling liquid droplets, which are very feebly doubly-refracting. The needles A at once show a tremendous number of transversal clefts, whilst the splendour of the colours diminishes strongly; A passes here into a second modification B, the common form of lupeol. Meanwhile the horny mass has also burst and exhibits here and there a strained double refraction besides an increase in the number of droplets, that is to say, crystallisation nuclei in an embryonal condition. If *heated* carefully for a moment, it *crystallises* into the needles A, which pass immediately into B (by bursting etc.); the horny mass A' is *identical* with the needles A: it is A in a *supercooled condition*.



The crystallisation velocity is here nearly $= 0$, and by heating it is increased to such an extent (owing to the diminution of the internal friction etc.) that the mass begins to crystallise. This is a phenomenon well known to me; beautiful instances of crystallisation on heating are usnic acid and many cholesterol esters of fatty acids.

On remelting B, A is formed some times for a few short moments, afterwards L. The two modifications therefore appear to be related by enantiotropy."

Utrecht, Org. Chem. Lab. Univers.

Statistics. — *"Relations between mortality of infants and high temperatures."* By Dr. E. VAN EVERDINGEN. (Communicated by Prof. C. H. WIND.)

In the "Statistische mededeelingen uitgegeven door het bureau van statistiek der gemeente Amsterdam" the other day a treatise appeared as N° 19: "Kindersterfte in Nederland (in de jaren 1881—1905)" by Prof. Dr. R. H. SALTET and Mr. PH. FALKENBURG.[1]) The authors point to the fact of the existence of a distinct maximum in the mortality of children under one year of age in the summer-months, and try to find among others a relation between the amplitude of this maximum in different places and in different periods, and the monthly means of temperature at neighbouring places in the same periods. The result is rather negative; hence they write as follows:

"Also from the chronological comparison of the mortality of infants and temperatures, as given by us here for Zealand and the town of Groningen, we are only able to draw a negative conclusion. If in a single case we may speak of parallelism, in the majority of the cases no direct relation between temperatures and mortality of infants can be traced. In so saying we do not imply that we have proved the statement, that the mortality of infants should be independent of the condition of the air. On the contrary, the diagrams we gave furnish the most evident proofs of a relation between the condition of the air in the summer and the mortality of infants. But it is not the height of the temperature which regulates this mortality. As we remarked before, in our opinion the probability remains, that the temperature-fluctuations of the summer — diurn or interdiurn — are the causes which exert an obnoxious influence. The data concerning these fluctuations fail however and cannot in our opinion be replaced by data about temperature-frequencies, which the Meteorological Institute would be able to furnish. We cannot but with a single word refer here to the theory which connects the summer mortality of babies with the presence in this season of a larger number of insects, bearers of disease-germs. Positive facts enabling to further investigate this matter are lacking at present.

Hence there is reserved here a vast field of research for the zealous investigator of the future.

---

1) A german translation of this treatise appeared under the title: "Statistische Mitteilungen des Statistischen Amtes der Stadt Amsterdam N°. 19. Kindersterblichkeit besonders in den Niederlanden, bearbeitet von Prof. Dr. R. H. SALTET and Dr. PH. FALKENBURG.

2. We think we can show that the writers have expressed themselves here in too definite terms, and that a distinctly positive result is obtained if another method of research is followed.

Already in furnishing the mean monthly temperatures for periods of 5 years, which the writers used for their research, the present writer expressed his doubt as to whether these data were fitted for the purpose aimed at. If the fluctuations of the mortality of infants were merely directly proportional to the fluctuations of the mean monthly temperature, the relation sought for ought indeed to appear also in this way. As soon however as these data are otherwise connected — e.g. the increased mortality occurs only after the temperature exceeding a certain limit — it is no longer allowed to use mean values without further inquiry.

The research of Prof. SALTET and Mr. FALKENBURG did indeed not, as we saw before, reveal any relation between mean monthly temperatures and mortality of infants. We will demonstrate this here clearly once more by giving for a single town, Groningen, the deviations from the mean for 25 years of the 5-annual means of the mortality of infants in the summer months May-September, and by their side, in italics, the same deviations for the temperature. The former are given in hundredths per diem, the latter in tenths of a degree Celsius.

GRONINGEN 1881—1905.

Period	May		June		July		Aug.		Sept.	
1881—1885	10	—5	12	— 9	32	1	0	— 8	—9	—4
1886—1890	9	3	17	1	24	—11	— 1	— 6	9	— 2
1891—1895	3	5	—10	—10	—'8	— 1	—13	4	—2	4
1896—1900	—14	—5	— 5	15	—20	6	9	11	4	3
1901—1905	— 7	2	—17	4	—16	6	6	— 2	—4	—2

If high temperature-means for 5-year-periods were accompanied by high mortalities of infants, at least the signs of the two kinds of deviations ought to agree generally. We find however 12 concordances, 12 discrepancies and 1 undecided case; hence in this way no relation is apparent.

3. It might be supposed that this very unfavourable result is caused partly by adding up the numbers for five years. In this connection we might mention that Dr. OLLAND [1]) formerly traced a

[1]) A. G. OLLAND, Invloed van het weer op het sterftecijfer. Thesis, Utrecht. 1896.

difference in the general mortality by comparing very hot and very cold summermonths. The principal causes however are different.

We now take as an example the mean mortality of infants at Groningen over the whole period 1891—1905, expressed for every month in percentages of one twelfth of the year-mortality; then we find in round percentages (l.c. p. 74, Table XLIII B).

April	May	June	July	Aug.	Sept.	Oct.
103	93	100	110	133	103	83

We will compare these numbers with the mean monthly temperatures, and moreover with the number of days with excessively high temperatures, which occurred during a similar period. In this respect we think in the first place of the days with maximum temperatures above 25° C., for which the normals occur in the "Maandoverzicht der weersgesteldheid in Nederland"[1]).

We thus find for the total number during the period 1894—1906.

April	May	June	July	Aug.	Sept.	Oct.
2	20	64	100	51	22	1

whereas the mean monthly temperatures in the period 1891—1905 are

8.6	13.0	16.6	18.4	17.6	14.7	9.6

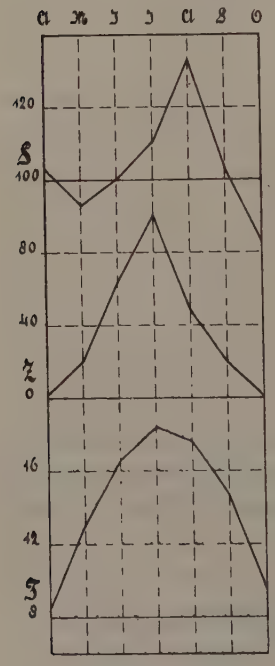


Fig. 1.

There is much more resemblance between the form of the maxima in the first two series of numbers than between those of the first and third series, as is clearly shown by fig. 1. (S mortality, Z number of days with max. temp. $> 25°$, T mean monthly temperature); but also for the second series the epoch of the maximum does not coincide with that of the first: it seems as if there is a retardation of the mortality as compared with the high temperatures.

In itself this does not look improbable. Though the writer enters here a field where he is scarcely entitled to a judgment, he thinks he may risk the supposition, that perhaps the high temperatures favour the development of diseases which only after a certain lapse of time cause death. If this be the case, then a better agreement between the fluctuations of temperature and mor-

[1]) (Monthly weather review in the Netherlands) Publ. N°. 94 Kon. Ned. Meteor. Inst.

tality must be obtained if the latter are compared with mean temperatures or numbers of days with high temperatures for a period which begins and ends a little earlier.

We have tested this conclusion by calculating the mean temperatures as well as the numbers of days with temperature above 25° — which, in accordance with a terminology used in meteorology, we will call henceforth "summer days" — once for the calendar months, once for periods from the 16th of one month till the 15th of the next month.

Both the choice of the "shift" of 15 days and that of the temperature-limit 25° are somewhat arbitrary. For a preliminary research like ours there is however no objection to this. From the table below it appears that at least for some parts of our country the shift has about the size which serves the purpose; by *S* are indicated the mean values of the mortality of infants for calendarmonths during the period mentioned in the first column, given in percentages of one twelfth of the yearly death-rate, as we will continue doing in the following pages; by *T* the mean numbers of summerdays in 5 years, for periods of one month shifted over 15 days.

Period	Place of observation	May-June	June-July	July-Aug.	Aug.-Sept.
1891—1905	*S* Groningen	100	110	133	103
	T Groningen	19	21	32	16
1881—1905	*S* Utrecht	102	130	133	97
	T Utrecht—de Bilt	18	25	22	15
1881—1905	*S* Zealand	72	101	159	159
	T Flushing	4	12	12	7

For Groningen and Utrecht the maxima now coincide wholly or almost so. For the province of Zealand, only partially well represented as to its climate by Flushing, a difference of a month in the epoch of the maximum remains.

4. We first give here the results of the investigation for Groningen, in which we compare successively with the deviation of the mortality in 5-year periods the deviations of:

a. the common mean monthly temperatures;

b. the means for the periods May 16th—June 15th etc.;

c. the numbers of summerdays for calendarmonths;

d. the number of summerdays for the periods May 16th—June 15th etc.

GRONINGEN 1881—1905.

Period	June		July		Aug.		Sept.	
			a. Mean temperatures for calendarmonths					
1891—1895	—3	*—13*	—5	*—5*	—28	*0*	—7	*2*
1896—1900	7	*12*	—6	*2*	10	*7*	5	*1*
1901—1905	—4	*1*	11	*2*	19	*—6*	2	*—4*
			b. Mean temperatures May 16th—June 15th etc.					
1891—1895	—3	*—7*	—5	*0*	—28	*— 7*	—7	*4*
1896—1900	7	*3*	—6	*—2*	10	*8*	5	*5*
1901—1905	—5	*3*	11	*2*	19	*—2*	2	*—8*
			c. Summerdays calendarmonths.					
1891—1895	—3	*—11*	—5	*—12*	—28	*1*	—7	*—2*
1896—1900	7	*14*	—6	*6*	10	*2*	5	*3*
1901—1905	—4	*— 2*	11	*6*	19	*—3*	2	*—1*
			d. Summerdays May 16th—June 15th etc.					
1891—1895	—3	*—7*	—5	*—1*	—28	*—16*	—7	*5*
1896—1900	7	*8*	—6	*—2*	10	*9*	5	*2*
1901—1905	—4	*—2*	11	*3*	19	*7*	2	*—8*

First regarding only the signs, we find:

	concordances	discrepancies	Undecided
a	6	5	1
b	7	4	1
c	8	4	—
d	10	2	—

The differences between a and b, and between c and d give the effect of the substitution of number of summerdays for mean-temperatures, the differences between a and b, and between c and d the effect of a shift of 15 days. It appears that the improvement in the concordance of the signs is largest for the transition from b to d; in the transition from c to d in the first place the improvement also in the quantitative agreement of the deviations of mortality and number of summerdays is remarkable. Finally the agreement in case d may be called so satisfactory, that but little doubt remains whether the high temperatures must be considered as the cause of the increased mortality of infants.

Hence the negative result arrived at by Prof. SALTET and Mr. FALKENBURG was due partly to the use of mean temperatures instead of temperature frequencies, partly to their non considering a retardation of the mortality with respect to the cause of death.

We will now test the agreement in case d also for Utrecht and Zealand.

UTRECHT (de Bilt).

Period	June		July		Aug.		Sept.	
1881—1885	16	— 7	17	10	—29	— 3	—13	— 4
1886—1890	15	— 4	—22	—11	—11	—14	— 2	1
1891—1895	—10	— 2	—10	— 7	— 6	—10	— 2	1
1896—1900	— 7	8	7	4	8	21	15	8
1901—1905	—21	5	7	6	46	8	3	— 6

ZEALAND (Flushing)

Period	June		July		Aug.		Sept.	
1881—1885	— 3	1	11	9	21	3	—12	— 3
1886—1890	4	2	3	— 4	—30	— 3	7	0
1891—1895	9	0	4	— 1	—12	—10	— 8	1
1896—1900	—13	— 1	—11	— 5	21	7	38	7
1901—1905	4	0	— 7	0	1	4	—24	— 5

Hence so far as the signs are concerned we find:

	Concordance	Discrepancy	Undecided
Utrecht:	13	7	—
Zealand:	12	4	4

The number of concordances in these cases is large enough to show that the fluctuations in the number of summerdays play an important part in the matter of the mortality of infants, especially if we consider that at Utrecht as well as in Zealand most concordances occur in the months of large mortality of infants: July and August for Utrecht, August and September for Zealand. Doubtless there are besides them other important circumstances, not connected with temperature, the influence of which even in means for 5 years is not yet eliminated. This need not surprise us — it rather may be called remarkable that in the case of Groningen not *more* is shown of such circumstances. Whether a better agreement might be obtained by assuming a higher temperature limit for Utrecht, for Zealand a lower temperature limit and another value for the shift we have not tried so far.

The mean temperatures for the periods May 16th—June 15th etc. were not calculated for Utrecht—de Bilt and Flushing; a comparison of the methods *a*, *c* and *d* however favours the view, that no improvement would ensue. For, the result for Utrecht was:

	Concordance	Discrepancy	Undecided
a	13	7	—
c	13	6	1
d	13	7	—

for Flushing

a	7	7	6
c	12	7	1
d	12	4	4

It would seem as if the result for Utrecht is practically the same in the three cases. If however also the quantitative agreement is considered, this appears to be wholly lacking in the case *c*, but to be much better in case *d* than in case *a*; hence the results obtained for Groningen are also here, though not so generally, valid.

5. A drawback of the use of means or sums for periods of 5

years is this, that the total number of data for comparison is rather small, and that there remains an uncertainty as to whether really the increased mortality, appearing from these means, occurred in the *same* years in which also the number of summerdays was largest. For this reason we have compiled from the "Ned. Staatscourant" the numbers expressing the death-rate of children less than one year of age for the period 1881—1905, both for Utrecht and Groningen; we have expressed the monthly values in percentages of one twelfth of the yearly death-rate, and compared these data after the method of the preceding §§, by comparing the deviations from the means for the period 1881—1905 respectively 1891—1905, with the deviations of the number of summerdays between May 16th and June 15th etc.

The results are given in the following tables.

GRONINGEN 1891—1905.

Year	June		July		Aug.		Sept.	
1891	— 4	—4	— 32	—1	—47	—5	0	—2
92	35	2	—26	—5	— 9	—4	2	2
93	—26	—2	12	5	—22	—2	—37	4
94	—39	—2	2	—1	— 61	—1	— 7	—3
95	25	—2	11	0	4	—2	13	5
96	41	3	48	2	—15	2	—44	—3
97	— 2	4	—12	0	24	1	7	—3
98	— 7	—1	—67	—6	42	—2	— 2	5
99	— 3	—2	8	3	—33	5	— 8	2
1900	12	3	—11	—2	36	5	61	2
01	— 5	—3	10	3	2	13	—30	0
02	48	2	—21	1	—30	—5	— 9	—2
03	—11	0	—15	—3	1	—4	33	—1
04	—21	0	13	—4	134	5	18	—1
05	—38	—2	75	5	—21	0	6	—3

UTRECHT 1881– 1905.

Year	June		July		Aug.		Sept.	
1881	9	— 3	—14	2	—12	1	— 9	— 3
82	—17	— 3	3	— 3	—49	— 2	10	— 3
83	35	— 2	0	3	—61	— 3	— 9	— 1
84	25	— 4	35	7	7	6	—40	5
85	39	3	12	1	—41	— 3	—15	— 2
86	26	— 1	—35	— 3	—15	— 2	43	10
87	23	— 4	—17	— 1	— 9	0	—25	— 1
88	— 9	— 1	—21	— 1	—29	— 2	—27	— 3
89	27	4	16	— 1	— 8	— 4	10	— 2
90	21	— 4	—45	— 5	— 3	— 2	—15	— 2
91	—21	— 4	—28	— 3	—15	— 2	— 8	— 2
92	3	4	—22	— 4	—42	— 3	16	2
93	1	0	18	4	40	0	—21	2
94	—12	— 2	10	— 1	0	— 1	—17	— 3
95	— 4	— 2	— 6	— 2	—14	— 2	21	2
96	3	0	0	4	—13	1	8	— 3
97	17	6	19	4	0	6	— 6	— 2
98	3	2	—33	— 5	15	— 1	57	8
99	—46	— 1	27	2	14	8	13	3
1900	— 8	3	41	— 1	18	9	— 5	2
01	—17	0	20	1	21	9	—12	0
02	— 9	1	—40	1	—48	— 3	11	— 1
03	—25	3	—18	1	18	— 3	27	0
04	—45	— 1	35	— 2	174	7	6	— 2
05	— 8	0	44	5	36	0	—17	— 3

For comparison we give the same table, with the mean temperatures at Groningen for the periods May 16th—June 15th etc. (case *b* § 4). The deviations for these temperatures are given in tenths of degrees.

GRONINGEN 1891—1905 *(b)*.

Year	June		July		Aug.		Sept.	
1891	— 4	—23	—32	2	—47	— 9	—27	3
92	35	9	—26	—16	— 9	—17	4	10
93	—26	6	12	13	—22	— 4	—35	7
94	—39	—18	2	3	—61	— 1	— 5	—19
95	25	— 6	11	— 4	4	— 3	15	20
96	41	11	48	6	—15	1	—42	— 1
97	— 2	27	—12	2	24	12	9	— 8
98	— 7	— 9	—67	—22	42	— 5	0	25
99	— 3	—13	8	9	—33	14	— 6	5
1900	12	3	—11	— 4	36	15	63	3
1	— 5	— 4	10	2	2	21	—28	— 8
2	48	— 2	—21	2	—30	—29	— 7	— 6
3	—11	0	—15	—14	1	—15	35	—13
4	—21	8	23	— 4	134	13	20	— 4
5	—38	10	75	24	—21	1	8	— 8

It was to be expected that in these tables more cases would be found where the signs do not agree, or the magnitude of the deviation in one series of numbers is not proportional to that in the other series; indeed, all disturbing causes exert their full influence here. If however we leave out of consideration those cases where one of the deviations is zero, and those where the deviation of the number of summerdays is but one, or the deviation of the mean temperature not more than 0.°2 (Groningen *b*) then we obtain the following résumé:

Signs equal.				Signs opposite.		
Number of cases	Sums			Number of cases	Sums	
	T	*S*			*T*	*S*
31	114	927	Groningen	13	42	191
50	186	1275	Utrecht	19	54	308
31	38,4	836	Groningen (b)	17	14,9	366

Hence in the two first tables the number of concordances is much larger than that of the discrepancies, and, moreover, in the favourable cases the mean deviations of number of summerdays and mortality are greater, so that in our opininion no doubt remains concerning the relation between the two phenomena.

The résumé for the third table clearly shows that the parallelism with the deviations of the mean monthly temperatures is not so good as with the number of summerdays.

We may now try to find the factor, which can express this relation approximately. For this purpose we take the sum of all positive deviations of the number of summerdays, and compute the algebraic sum of the corresponding deviations of the mortality of infants. Likewise for the negative deviations of the summerdays. We thus find:

	Sum pos. dev. T	Sum S	Sum neg. dev. T	Sum S
Groningen	+ 81	+ 463	— 83	— 352
Utrecht (town)	+ 120	+ 502	— 120	— 465

Without giving all numbers in detail we may add here the result for the province of Utrecht, where 54 concordances occur against 17 discrepancies:

Utrecht (prov.)	+ 133	+ 543	— 118	— 433

The difference between sum S for positive and negative deviations of T, rather large for Groningen, is probably an indication of a non linear relation. If we overlook this and combine the two kinds of deviations, we find for the factor sought for Groningen about 5.0, for Utrecht (town) about 4.0, Utrecht (prov.) about 3.9.

6. What precedes still leaves open to doubt whether the high temperatures themselves cause the increased mortality, or, as Prof. Saltet and Mr. Falkenburg supposed, temperature-fluctuations connected with them. It might indeed be imagined that, as a rule, numerous high temperatures would be accompanied by numerous large temperature fluctuations. Though, from a meteorological point of view, this supposition did not look very probable, we have tested it likewise, for which purpose the annals of the Royal Netherlands Meteor. Institute are quite sufficient. For the same periods from the middle of one month to the middle of the next for which the summerdays had been counted, we computed for Groningen the sum of the differences of the maximum temperature from one day to another, for simplicity neglecting the tenths of degrees. The results were dealt with in the same way as before: hence the deviations of the

temperature fluctuation sums are expressed in entire degrees. The result follows here:

GRONINGEN 1891—1905.

Period	June		July		Aug.		Sept.	
1891—1895	— 3	—19	— 5	22	—28	—16	— 7	20
1896—1900	7	31	— 6	9	10	45	5	— 1
1900—1905	— 4	—11	11	—31	19	—30	2	—18

Among 12 cases there is concordance in 5, discrepancy in 7 cases, so that in this way no relation between the temperature-fluctuations from day to day and the fluctuations of the mortality of infants is shown. Also the annual range of the mean amplitude of the temperature-fluctuations from day to day has another character than that of the frequency of high temperatures; the maximum of the temperature-fluctuations falls in June, not in August. Therefore we thought it useless to separately investigate the *large* or the diurn temperature-fluctuations.

7. In concluding our investigation we are well aware that it is far from complete and leaves room for various questions. If we succeeded in convincing the reader that one of the prominent causes of increased mortality of infants is an increase of the number of very hot days, we express a hope that others, may it be competent in medical matters, will feel inclined to trace the more direct relations, to explain the different character of the phenomenon in various parts of the country, perhaps with the aid of other temperature limits and other shifts. The data the Meteorological Institute is able to furnish for this purpose, also concerning other elements than temperature, will readily be put at the disposal of the future investigator.

The results obtained so far may be summed up as follows:

1st. The fluctuations of the mortality of infants bear hardly any relation to those of the mean monthly temperatures in the same months, neither with those of the mean amplitude of the temperature-fluctuations from day to day.

2nd. The number of days with maximum temperature above

25° C. ("summerdays") counted for periods from May 16th to June 15th, June 16th—July 15th etc shows fluctuations, which in a large majority of cases agree in sign with those of the mortality of infants in June, July etc.

3rd. If a simple proportionality is assumed between the deviation from the normal of the number of "summerdays" and that of the mortality in a period beginning and ending 15 days later, then for each summerday above or below the normal number the mortality of infants is increased or diminished at Groningen with 5, at Utrecht with 4% of the mean monthly death-rate.

Chemistry. — "*Action of potassium hypochlorite on cinnamide*", (2nd communication). By Dr. R. A. WEERMAN. (Communicated by Prof. S. HOOGEWERFF).

It has been stated in a previous communication [1]) that from cinnamide and potassium hypochlorite was obtained cinnamoylstyrylurea.

$$\begin{matrix} C_6H_5C^H = C^H - N^H \\ C_6H_5C^H = C^H - C^O - N^H \end{matrix} \diagdown\!\diagup CO.$$

This proved that in the action of potassium hypochlorite on cinnamide an intramolecular rearrangement of atoms takes place, and that it therefore becomes possible to arrive from a compound with the atomic grouping:

$$C_6H_5C = C - C - N$$

at one with the atomic grouping:

$$C_6H_5C = C - N - C.$$

A compound of this structure may be very readily obtained from cinnamide by treating this in methylalcoholic solution with an alkaline solution of potassium hypochlorite. In this way a yield of about 70% of the urethane is obtained:

$$C_6H_5C^H = C^H - N^H - C^O{}_{OCH_3}$$

styrylaminoformic methyl ester.

B. p. 181°—182° at 14 mm. M. p. 122°—123° (corr.)

0,1674 gr. yielded 0,0914 gr. H_2O and 0,4141 gr. CO_2

0,1733 „ „ 12 cc. N_2 at 14° and 761 mm.

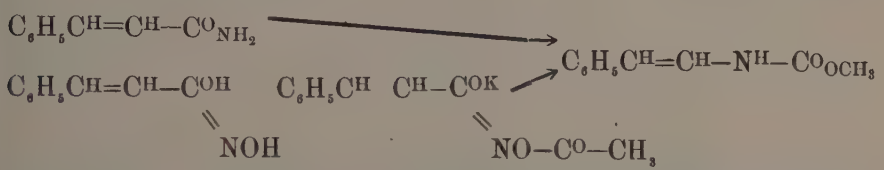
Found: 67,45% C; 6,11% H and 8,12% N.

Calculated for $C_{10}H_{11}O_2N$: 67,76% C; 6,27% H and 7,91% N.

[1]) Proc. 1906, 303.

A substance of the same structure has been described by THIELE and PICKARD [1]), who prepared it from the potassium salt of the acetylated cinnamo-hydroxamic acid. As they give the melting point as 115°, and as, in another respect, their observations do not quite agree with mine, the urethane was prepared by Mr. W. OCHTMAN, in the manner indicated by THIELE and PICKARD for the purpose of comparison.

The two substances appeared to be quite identical; the melting point was found to be 122°—123° and a mixture of the two melted at the same temperature.



This ready formation of urethane in an aqueous-alcoholic alkaline medium is remarkable.

I ascertained that this reaction also takes place with a derivative of cinnamic acid. From o-nitro-cinnamide is formed the o-nitrostyryl-aminoformicmethyl ester:

$$C_6H_4NO_2 - CH = CH - NH - CO_{OCH_3}$$

This crystallises in bright yellow needles mp. 149°—150°.

0,2009 gr. yielded 0,3956 gr. CO_2 and 0,0781 gr. H_2O.
0,1457 „ „ 15,8 cc. N_2 at 15° and 758 mM.

Found: 53,70 % C; 4,36 % H and 12,60 % N.
Calculated for $C_{10}H_{10}O_4N_2$: 54,03 % C; 4,55 % H and 12,61 % N.

A fuller communication will follow in the Receuil.

Delft, July 1907.

Chemical Laboratory of the Technical High School.

Meteorology. — *"The analysis of frequency-curves of the air-temperature."* By Dr. J. P. VAN DER STOK.

1. The question in what way the characteristic details of frequency-curves of different kinds may be pointed out in a striking way in a pliant, analytical form has again been treated extensively in a recent work [2]).

The aim of this communication is to fix the attention on the

[1]) Ann. 309, 197.

[2]) H. BRUNS, Wahrscheinlichkeitsrechnung und Kollektivmasslehre, Leipzig und Berlin, TEUBNER, 1906.

method of treatment suggested in it and to give some applications of it to frequency-numbers concerning air-temperature, deduced from observations made on board the lightship "Schouwenbank".

2. The method suggested by BRUNS deserves the more the consideration of all who are occupied with the treatment of frequencies as it is based on the classical works of BESSEL and FECHNER and can be regarded as a logical outcome of the principles indicated by these investigators.

As a basis is taken the well-known function

$$\Phi_0(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\, dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for which in various works tables are given; the first derivative of this function:

$$\Phi_1(x) = \frac{2}{\sqrt{\pi}} e^{-x^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

assumes after substitution of hx for x and multiplication by h the form of the specific probability of a deviation x according to the law of errors of GAUSS in its simplest form. The derivatives of higher order can be written thus:

$$\left.\begin{aligned}
\Phi_2(x) &= \frac{2^2}{\sqrt{\pi}} e^{-x^2} \cdot 1! \left[- \frac{x}{0!\,1!} \right] \\
\Phi_3(x) &= \frac{2^3}{\sqrt{\pi}} e^{-x^2} \cdot 2! \left[\frac{x^2}{0!\,2!} - \frac{1}{1!\,0!\,2^2} \right] \\
\Phi_4(x) &= \frac{2^4}{\sqrt{\pi}} e^{-x^2} \cdot 3! \left[- \frac{x^3}{0!\,3!} + \frac{x}{1!\,1!\,2^2} \right] \\
\Phi_5(x) &= \frac{2^5}{\sqrt{\pi}} e^{-x^2} \cdot 4! \left[\frac{x^4}{0!\,4!} - \frac{x^2}{1!\,2!\,2^2} + \frac{1}{2!\,0!\,2^4} \right] \\
\Phi_6(x) &= \frac{2^6}{\sqrt{\pi}} e^{-x^2} \cdot 5! \left[- \frac{x^5}{0!\,5!} + \frac{x^3}{1!\,3!\,2^2} - \frac{x}{2!\,1!\,2^4} \right]
\end{aligned}\right\} \quad (3)$$

etc.

Now BRUNS' suggestion is as follows: the specific probability (sum of the numbers $= 1$) of a deviation from a groundvalue assumed arbitrarily be represented by the series:

$$y = h\,[D_0\Phi_1(hx) + D_1\Phi_2(hx) + D_2\Phi_3(hx) + \ldots .] \quad . \quad . \quad . \quad (4)$$

from which ensues, that the integral of this equation, called the curve of the sums, is expressed by the form

$$D_0\Phi_0 + D_1\Phi_1 + D_2\Phi_2 + \text{etc.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where Φ means $\Phi(hx)$, as is the case in what follows.

From (4) it is immediately evident when regarded in connection with (3) that the suggested analysis of the curve (called by BRUNS not frequency-curve but curve of distribution) shows a resemblance to the development of a function in terms of a FOURIER series.

In the different Φ_p terms appear polynomial functions of order $p-1$; the Φ_p curve shows p maxima and minima and intersects the x axis in $p-1$ points and alternately will be found for $x = 0$ either an extreme value (order uneven) or a point of intersection (order even).

The constants D are determined in the well-known way by evaluating the moments of various orders with respect to the y-axis through the origin of coordinates; if we take for this origin the value of x corresponding to the arithmetical mean and if we put:

$$\int_{-\infty}^{\infty} x^n y \, dx = \mu_n ,$$

we find evidently $D_0 = \frac{1}{2}$ on account of μ_0 being equal to 1; furthermore μ_1 must be $= 0$ on account of the choice of the origin, so D_1 must be put equal to 0, whilst, if one defines the value of the constant h in such a way that

$$2h^2\mu_2 = 1 ,$$

it is then easy to deduce that also D_2 must be 0.

The expressions (4) and (5) can thus be simplified and they become

$$y = h[\tfrac{1}{2}\Phi_1 + D_3\Phi_3 + D_4\Phi_4 \ldots] \quad . \quad . \quad . \quad . \quad (4^a)$$

and

$$\tfrac{1}{2}\Phi_0 + D_3\Phi_3 + D_4\Phi_4 \ldots \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5^a)$$

The constants D_3, D_4, etc. can easily be calculated by means of the formula (3) where, with a view to this, the above mentioned form is given.

To calculate $2D_n$ we have namely, to consider the form appearing between square brackets in the expression for Φ_{n+1} and to substitute in it $h^n\mu_n$ for x^n.

Our finding in this way $2D_n$ instead of D_n is due to the same reason why D_0 must be put equal to $\frac{1}{2}$; namely to the form of (1) in which the number 2 stands as coefficient.

TABLE I.

Air temperature. Schouwenbank. Frequencies of Daily-means.

Celsius	January	February	March	April	May	June	July	August	September	October	November	December
−8.9° to −8.0°	1	—	—	—	—	—	—	—	—	—	—	1
−7.9 −7.0	—	1	—	—	—	—	—	—	—	—	—	—
−6.9 −6.0	—	1	—	—	—	—	—	—	—	—	—	1
−5.9 −5.0	2	2	—	—	—	—	—	—	—	—	1	—
−4.9 −4.0	2	3	—	—	—	—	—	—	—	—	—	3
−3.9 −3.0	5	5	—	—	—	—	—	—	—	—	1	7
−2.9 −2.0	18	14	3	—	—	—	—	—	—	—	—	10
−1.9 −1.0	32	23	6	—	—	—	—	—	—	—	3	27
−0.9 0.0	53	37	15	—	—	—	—	—	—	—	2	21
0.1 1.0	56	48	25	—	—	—	—	—	—	—	—	27
1.1 2.0	77	89	50	—	—	—	—	—	—	—	13	39
2.1 3.0	112	123	69	8	—	—	—	—	—	—	23	85
3.1 4.0	134	134	111	13	—	—	—	—	—	—	30	77
4.1 5.0	150	176	150	36	—	—	—	—	—	—	45	101
5.1 6.0	147	142	202	96	—	—	—	—	—	1	55	163
6.1 7.0	113	111	157	167	11	—	—	—	—	6	81	163
7.1 8.0	70	82	95	206	36	4	—	—	—	28	131	122
8.1 9.0	24	10	69	186	112	3	—	—	—	57	158	91
9.1 10.0	4	—	25	142	161	3	—	—	—	73	158	48
10.1 11.0	—	—	15	97	215	19	—	—	4	105	167	14
11.1 12.0	—	—	2	45	166	71	—	—	6	194	86	—
12.1 13.0	—	—	6	3	130	165	8	—	51	189	41	—
13.1 14.0	—	—	—	1	87	180	27	4	67	182	4	—
14.1 15.0	—	—	—	—	46	218	85	49	149	87	1	—
15.1 16.0	—	—	—	—	32	160	170	152	222	53	—	—
16.1 17.0	—	—	—	—	4	94	275	254	230	18	—	—
17.1 18.0	—	—	—	—	—	57	215	245	152	3	—	—
18.1 19.0	—	—	—	—	—	19	130	137	71	4	—	—
19.1 20.0	—	—	—	—	—	7	64	106	29	—	—	—
20.1 21.0	—	—	—	—	—	—	24	32	15	—	—	—
21.1 22.0	—	—	—	—	—	—	1	15	4	—	—	—
22.1 23.0	—	—	—	—	—	—	1	3	—	—	—	—
23.1 24.0	—	—	—	—	—	—	—	3	—	—	—	—

For the values of Φ_1, Φ_2 .. Φ_6 BRUNS has given tables, so there are no further difficulties about the calculations which can easily be done after some practice.

We must suffice with this short and for that reason incomplete survey of the method; for further details we must refer to the above-mentioned work, where all questions which may arise are discussed extensively.

3. When applying this method to observations of air-temperature it has been assumed that the series need not be continued farther than to the third term, so that only asymmetrical (D_3) deviations and symmetrical ones (D_4) of order one of the simple law are regarded, which, with these kinds of curves not differing much from the bell-shape, proves to be sufficient. When introducing terms of higher order the disadvantage moreover appears that with the evaluation of the higher moments the single extreme deviations, therefore inaccurately determined, play an unduly important part. As first example have been selected the daily-means of the air-temperature, because with these frequency-curves their obliquity changes sign along with the season and can therefore be regarded as a climatological factor. The daily-means are calculated from observations on temperature taken six times a day during the years 1882—1904.

In Table I the frequencies are given from degree to degree, calculated at a total of 1000; the number of data amounts of course for every month to about:

$$23 \times 30 = 690 \text{ or } 23 \times 31 = 713.$$

The obliquity is immediately evident; in winter we find extreme temperatures or negative deviations which are not compensated by equally large positive deviations; in summer we find on the contrary important positive deviations not contrasted by negative ones. The constants of the curve, namely, the mean temperature M indicating the origin of coordinates, the factor of consistency h and the coefficients D_3 and D_4 by which the deviations of the curve from the regular bell-shape are determined are found in survey in Table II; the last two quantities having reference to $\mu_0 = 1$, so that they must still be multiplied by 1000 for the calculation of the numbers comparable to the frequencies of Table I.

TABLE II.

Constants of the frequency-curves.
Daily-means of air-temperature.

	M	h	D_3	D_4
January	3.762 C.°	0.2587	+ 0.01657	— 0.00043
February	3.842	0.2773	+ 0.01959	+ 0.00048
March	5.321	0.2908	+ 0.00214	+ 0.00213
April	7.953	0.3738	+ 0 00313	— 0.00115
May	11.068	0.3540	— 0.00847	— 0.00166
June	14.320	0.3708	— 0.00015	+ 0.00114
July	16.871	0.4442	— 0.00216	+ 0.00007
August	17.367	0.4380	— 0.01170	— 0.00026
September	16.032	0.3893	— 0 00634	+ 0.00106
October	12.142	0.3335	+ 0.00470	— 0.00002
November	8.399	0.2662	+ 0.02657	+ 0.00659
December	5.174	0.2377	+ 0.02463	+ 0.00390

From these results of the calculation it is evident that in contrast to most frequency-curves, the D_4 deviations from the simple exponential law for the frequency-curve of the daily-means of the air-temperature are slight and may be regarded as being within the limits of the errors of observation.

In order to investigate how far the calculation agrees with the observation, the numbers of Table I for the months of January and December are taken together as being the most asymmetrical. The numbers obtained in this way are indicated in Table III by O (observed).

The constants of these curve are:

$$M = 4.469 \text{ C}°$$
$$h = 0.2403$$
$$D_3 = + 0.01764$$
$$D_4 = + 0.00130$$

TABLE III.

Analysis of the frequencies Jan. + Dec. of Table I.

O	C_0	$O-C_0$	C_3	$O-C_0-C_3$	C_4	$O-\Sigma C$
1	0	1.0	0.1	0 9	—	1
0	0.1	— 0 1	0.2	— 0.3	0 1	0
0^5	0.2	0.3	0.3	0.0	0.2	0
1	0.4	0.6	1.3	— 0.7	0.3	— 1
2^5	1.4	1.1	2.5	— 1.4	0.4	— 2
6	3.4	2.6	4.0	— 1.4	0.4	— 2
14	8.4	5.6	5.0	0.6	0.1	1
29^5	17.5	12.0	3.7	8.3	— 0.9	9
37	32.9	4.1	— 0.3	4.4	— 2.0	6
41^5	54.9	— 13 4	— 8.7	— 4.7	— 2.5	— 2
58	81.5	— 23.5	— 16 0	— 7.5	— 1.7	— 6
98^5	108.0	— 9.5	— 25.2	15.7	0.6	15
105^5	127.9	— 22.4	— 11.9	— 10.5	3.1	— 13
125^5	134.9	— 9.4	0.4	— 9.8	4.1	— 14
155	127.0	28.0	12.6	15.4	2.9	13
138	106.6	31.4	18.2	13.2	0.5	13
96	79.7	16.3	15.7	0.6	— 1.8	2
57^5	53.3	4.2	8.2	— 4.0	— 2 6	— 1
26	31.7	— 5 7	0.6	— 6.3	— 1.9	— 4
7	16.9	— 9.9	— 3.9	— 6.0	— 0 8	— 5
—	8.4	— 8.4	— 5.0	— 3.4	0 1	— 4
—	3.0	— 3.0	— 3.9	0.9	0.4	1
—	1.2	— 1.2	— 2.4	1.2	0.5	1
—	0.3	— 0.3	— 1.2	0.9	0.3	1
—	0.3	— 0.3	— 0.5	0.2	0.1	0
—	0.1	— 0.1	— 0.2	0.1	0.1	0
$\Sigma = 1000$		$\Sigma = 214.6$		$\Sigma = 118.4$		$\Sigma = 117$

In the second column is given under C_0 (calculated) the distribution derived according to the simple exponential law; in the fourth column we find the values of the second term in the series having D_3 as factor; from the third and fourth columns is evident that the sum of the differences is lessened by this term from 215 to 118 a thousand. As has been noticed before, the influence of the third term with D_4 is slight.

The sum of the differences remains 12%, also after introducing this term, which can be called satisfactory considering that the total number of observations is not more than:

$$2 \times 31 \times 23 = 1426$$

and that the most unfavourable months have been taken as an example. In fact, from the regular course of the differences it is evident that there might be a possibility of making the differences smaller still by addition of a fourth or a fifth term with D_5 and D_6.

For D_5 we find the value — 0.00036, from which ensues that of by far the greater part the differences are due to incompleteness of the material of observation, so that extension of the series would avail but little.

4. As fitting material for a second application of the method to meteorological quantities all the observations of temperature have been chosen, taken six times a day in the month of July on the same lightship during the years 1882—1906. The number of observations is now six times greater than for the daily-means and amounts to 4516.

On account of this greater number the frequency-curve will have a more regular shape and the obliquity which was easily discernible for the daily-means also for the summer months, will now come more clearly to the front.

The observations are arranged according to the different quarters of the wind, so that we obtain (Table IV) frequencies of the so-called thermic windrose. On board the lightships the direction of the wind is determined in accordance with the indications of the compass; for the period 1882—1906 we can assume that these observed directions of the wind can be reduced to the proper direction by applying as correction the mean deviation, — 15°.

TABLE IV. Frequencies of air-temperatures for different quarters of the wind (Magnetic), Schouwenbank, July, 1882—1906.

	N	*NNE*	*NE*	*ENE*	*E*	*ESE*	*SE*	*SSE*	*S*	*SSW*	*SW*	*WSW*	*W*	*WNW*	*NW*	*NNW*	*C*	Total
10.6—11.5 C	1	—	—	—	—	—	—	—	1	1	—	—	—	1	—	—	—	4
11.6—12.5	4	1	1	—	—	—	—	—	0	0	—	—	1	0	3	13	—	23
12.6—13.5	29	17	5	1	2	2	—	—	1	1	2	2	0	2	13	25	—	102
13.6—14.5	44	26	12	2	11	4	5	4	3	4	15	11	9	20	43	51	3	267
14.6—15.5	71	49	35	21	18	9	13	4	13	9	30	66	69	72	77	49	18	623
15.6—16.5	67	66	80	41	27	14	18	18	19	27	70	164	152	73	50	42	24	952
16.6—17.5	56	38	79	39	35	18	28	15	37	31	94	182	147	51	44	37	37	968
17.6—18.5	34	29	56	38	32	23	25	15	22	22	62	140	119	31	41	26	27	742
18.6—19.5	26	13	48	16	27	13	16	7	14	14	35	67	52	13	21	10	27	419
19.6—20.5	9	10	29	16	16	6	13	4	5	10	19	17	24	6	9	6	18	217
20.6—21.5	4	4	18	10	10	1	6	6	5	4	2	5	6	1	6	3	7	98
21.6—22.5	2	2	7	3	2	4	4	3	3	1	4	2	5	1	2	1	15	61
22.6—23.5	2	2	3	3	1	0	2	1	1	0	1	—	1	0	2	1	4	24
23.6—24.5	—	1	1	0	2	1	—	—	—	1	3	—	—	0	—	—	1	10
24.6—25.5	—	—	1	1	1	—	—	—	—	—	—	—	—	1	—	—	1	5
25.6—26.5	—	—	—	—	1	—	—	—	—	—	—	—	—	—	—	—	—	1
Sum	349	258	375	191	185	95	130	77	124	125	337	656	585	272	311	264	182	4516

More clearly than in the numbers of Table IV does the influence of the direction of the wind on the temperature show itself in the mean temperature M and the factor of consistency h, arranged in Table V.

TABLE V.

Direction of wind Magn.	Number of observ.	Mean Temp. *M.*	*h*
N	349	13°.10	0.3485
NNE	258	16.33	0.3478
NE	375	17.50	0.3477
ENE	191	17.61	0.3561
E	185	17.68	0.3155
ESE	95	17.53	0 3491
SE	130	17.77	0.3527
SSE	77	17.67	0.3436
S	124	17.39	0.3713
SSW	125	17.38	0.3754
SW	337	17.23	0.4037
WSW	656	17.08	0.5124
W	585	17.10	0.4685
WNW	272	16.32	0.4391
NW	311	16.27	0.3512
NNW	264	15.65	0.3418
Calm	182	18.56	0.3295

From this table is evident that in this summermonth by far the highest temperatures are observed when there are calms; for the rest we have the lowest temperatures with the northerly seawind, the highest with a landwind; the transition from NNE (W 7°.5 E prop. dir.) to NE (N 30° E prop. dir.) is sharp, much sharper than that from SW (N 210° E prop. dir. landwind) to WNW (N 277°.5 E proper dir. seawind).

This sharp difference we do not find for the factor of consistency, which shows for WSW wind a distinct maximum and for calm a minimum.

The numbers of observations being rather slight for many directions

of the wind, the numbers of Table IV have been arranged in Table VI to five groups where as much as possible comparable series have been added together.

TABLE VI.

Frequencies deduced from Table IV.

	WNW — NNE	NE — E	ESE — SW	WSW — W	C	Total
10.6—11.5 C°.	2	—	2	—	—	4
11.6—12.5	21	1	0	1	—	23
12.6—13.5	86	8	6	2	—	102
13.6—14.5	184	25	35	20	3	267
14.6—15.5	318	74	78	135	18	623
15.6—16.5	298	148	166	316	24	952
16.6—17.5	226	153	223	329	37	968
17.6—18.5	161	126	169	259	27	742
18.6—19.5	83	91	99	119	27	419
19.6—20.5	40	61	57	41	18	217
20.6—21.5	18	38	24	11	7	98
21.6—22.5	8	12	19	7	15	61
22.6—23.5	7	7	5	1	4	24
23.6—24.5	1	3	5	—	1	10
24.6—25.5	1	3	—	—	1	5
25.6—26.5	—	1	—	—	—	1
Sum	1454	751	888	1241	182	4516

The comparatively low temperatures for WNW—NNE winds with a small factor of consistency (great distribution) in contrast to the high temperatures and small distribution for WSW—W winds is very clear from this table.

At the same time is evident from these data how the combination of series with different mean values decreases the obliquity in the total, so that we can expect that the obliquity factor D_s will be considerably smaller for the total series than D_3, calculated for the various series, which is confirmed by the following table.

TABLE VII.

Constants of the frequency-numbers of Table VI.

	M	h	D_3	D_4
WNW—NNE	16°.135	0.3576	— 0.01778	0.00385
NE–E	17.589	0.3428	— 0.01657	0.00343
ESE–SW	17.430	0.3710	— 0.01540	0.00477
WSW–W	17.089	0.4869	— 0.01300	0.00297
C	18.555	0.3295	— 0.01153	0.00108
Total	16.971	0.3603	— 0 01116	0.00331

The (negative) obliquity D_3 is therefore strongest for the northerly seawinds with low temperature and decreases further regularly with the azimuth counted from North through East. The symmetrical deviation D_4 is greatest for southerly winds and smallest for calms.

TABLE VIII.

Analysis of the frequencies of Table VI.

O	C_0	$O-C_0$	C_3	$O-C_0-C_3$	C_4	$O-\Sigma C$
1	2.6	— 1.6	— 3 5	1.9	2.9	— 1
5	8.7	— 3.7	— 4.4	0.7	1.0	0
23	27.2	— 4.2	— 3.3	— 0.9	— 3.6	3
59	65.5	— 6.5	4.5	— 11.0	— 8.8	— 2
138	122.7	15.1	15.1	0	— 6.1	6
211	178.4	32.6	14.7	17.9	7.3	11
214	201.2	12.8	— 0.5	13.3	15.4	— 2
164	175.8	— 11.8	— 15.3	3.5	6.4	— 3
93	119.2	— 26.2	— 14.5	— 11.7	— 6.5	— 5
48	62 7	— 14.7	— 4.0	— 10.7	— 8.9	— 2
22	25.5	— 3.5	3.6	— 7.1	— 3.0	— 4
14	8.1	5.9	4.3	1.6	1.1	1
5	2.0	3.0	2.3	0.7	1.7	— 1
2	0.4	1.6	0.8	0.8	0.8	0
1	0.0	1.0	0.2	0.8	0.3	1
$\Sigma = 1000$		$\Sigma = 144.2$		$\Sigma = 82.6$		$\Sigma = 42$

Let us remark here that a negative D_3 refers to the ascending slope of the curves on the left being steeper than the descending slope on the right and that a positive sign of D_4 means that small deviations appear in greater number than would be the case in accordance with the simple exponential law.

In order to show clearly the part played by the various terms of the series in the composition of the curve of distribution a comparison has been given in table VIII, as in table VI, of the observed and calculated frequency-numbers of the last series of table IV; the number of observations 4516 has here been reduced in the first column under O to 1000.

From this table is evident that if only a great number of observations is at hand, the frequency-curve of the air-temperature can be very satisfactorily determined by the three constants of the series of BRUNS, the total of the differences between observation and calculation amounting in round numbers to 4 %.

Anthropology. — *"Is red hair a nuance or a variety?"* By Prof. L. BOLK.

Concerning the anthropological importance of red hair the literature relating to it contains up till now little more than opinions based upon general impressions or suppositions, founded on statistical data, which when looked at more closely are open to more or less unfavourable criticism. There is in those opinions and suppositions a definite main current according to which it is generally assumed that a closer affinity of redhairiness exists to what, for the sake of brevity, I shall indicate as the blonde race, characterized as to the pigmentation by blonde hair and blue eyes.

The nature of the relation between blonde and red-haired people is expressed by TOPINARD [1]) as follows: the red-haired type has arisen from the blonde type "par une action des milieux". Also BEDDOE and RIPLEY, to mention the principal English and the best known American anthropologist, assume a closer connection between blonde and red hair. VIRCHOW looks upon the subject from a somewhat different standpoint, when he says that redhairiness probably arises in two manners, viz. by a decrease of pigment in brown hair or an increase in blonde hair [2]). This opinion of VIRCHOW is based upon

1) Éléments d'Anthropologie générale. Paris 1885 p. 334

2) Das jedoch scheint mir nicht unwahrscheinlich zu sein, dass es eine doppelte Art von Rothharigkeit giebt, von denen die eine als eine Steigerung des Pigments bei den Blonden, die andere als eine Verminderung desselben bei den Braunen anzusehen ist. Archiv für Anthrop. XVI Bnd. p. 338.

his statistics of the extension of redhaired people in Germany. Now it would not be difficult to prove that VIRCHOW was in no way entitled to such a conclusion on the ground of his statistics; his data were very incomplete and the relations found by him he himself calls "ganz unzutreffend". I intend to revert to this in another place, but would like to examine another side of VIRCHOW's conclusion somewhat more closely. For where he says that redhairiness arises, either by an increase or by a decrease of the hair-pigment, this implies that in VIRCHOW's opinion redhairiness is the consequence of quantitative difference, and that, in other words, this quality is consequently only a question of gradation. Moreover I do not wish to enter into the question whether VIRCHOW has a right to place blonde or brown over against each other as primary or pure hair-colours. Let it suffice for the present to state that VIRCHOW sees no contrast between red and blonde hair, but that the former is only a nuance, either of blonde or of brown. I know only one anthropologist who, in contradistinction to the great majority, raises his voice against the existence of a closer relationship between red and blonde hair, viz. AMMON, who in his Anthropology of the Baden population hazards the suggestion that the difference between blonde and red hair is not founded on a quantitative difference of the pigment, but on a qualitative distinction. So AMMON is more inclined to the opinion that in redhairiness not a nuance, but a variety renders itself manifest [1]).

In working up my anthropological material concerning the population of Holland I have naturally come to the question about the importance of redhairiness, and the conclusion at which I have arrived deviates from the general opinion. The extension of redhairiness in our country causes me to deny every closer relationship with the blonde race.

Let me begin by pointing out that the composition of our population is very favourable for an answer to this question. A few years ago I had the pleasure in this meeting to throw light upon the main features of the composition of our population from the so-called blonde and brown-haired race. And I could then establish how the composition of our population differs, if the northern part of our country is compared with the southern. The blonde type decreases regularly in a southern direction, going hand in hand with an increase of mixed types, and though of course in a smaller proportion, an increase of the pure brown type. The differences

[1]) Die von manchen Anthropologen beliebte Vereinigung der roten Haare mit den blonden, halten wir für unzulässig, denn die roten stehen in vielen Fällen den braunen näher und sind jedenfalls stärker pigmentiert, haben vielleicht ein Pigment von anderer Beschaffenheit. Zur Anthropologie der Badener. blz. 129.

between the northern and southernmost parts of our country are in the end rather considerable, and it is for this very reason that our population is so extremely fit to answer a question like this. If it should after all be true that redhairiness is more closely related to blondness, then the variation in the number of blondes cannot but cause a similar change in the number of redhaired people.

The materials for the following illustration have again been borrowed from my inquiry made at the time into the distribution of the colour of hair and eyes among the population of Dutch schools. On the schedules that were distributed for that purpose I distinguished four colours of hair: blonde, brown, red and black, and four colours of eyes: blue, grey, brown and brownish-green. The total number of children examined, amounted, with the exception of the Israelites, to 478.976. The total number of redhaired individuals among them is 11772, so that there are on an average 2.45% redhaired children. The figures from which this proportion has been borrowed, are high enough to consider this as the exact average.

The first question we shall answer is: in what proportion do red-haired persons occur in the different provinces of our country. This appears from Table I. In the first column is found the total number of the children examined in each province, in the last the number of red-haired ones among them, also in the proportion expressed by the percentage. What appears from this last column? Suppose that in round numbers the general average is 25 red-haired individuals in 1000 inhabitants, then we see that in four provinces: Friesland, Gelderland, N. Holland and Utrecht the same proportional number appears, that there occurs in Z. Holland only one in 1000, in Groningen 2 in 1000 and in Overijsel and Limburg 3 in 1000 less — in N. Brabant 1 and in Drenthe 2 more in 1000 inhabitants. These figures differ so little, also from the general average, that we are in my opinion fully entitled to conclude that in the provinces mentioned the extension of red-haired persons is much the same everywhere.

This slight difference in the percentage of redhaired persons in our country is corroborated by Table II in which the absolute numbers and the proportions are mentioned of all the places in our country in which the number of the children examined was more than 2500. It was to be expected that where the absolute numbers are sometimes relatively low here, the variation of the percentage would be greater. But yet nowhere does the proportion fall below 2% and only once a percentage of 2.9 is reached as the most favourable proportion. Where the absolute figures are high, as in Amsterdam and Rotter-

TABLE I.

Province	Total	Blondhaired-blue-eyed	Blackhaired brown-eyed	Redhaired
Friesland	33.053	14.282=43.2%	566=1.7%	857=2.5%
Groningen	32.223	13.401=41.3	446=1.4	755=2.3
Drenthe	15.169	5.959=39.4	205=1.3	422=2.7
Overijsel	41.389	14.713=35.5	689=1.6	919=2.2
Gelderland	46.786	16 078=34 4	1340=2.8	1198=2.5
Zuid Holland . . .	108.073	33.943=31 4	2.712=2.5	2640=2.4
Noord Holland . .	97.050	30.291=31.2	1791=1.8	2472=2.5
Utrecht	22.017	6.626=30.1	528=2.4	545=2.5
Zeeland	20.986	5.707=28.4	834=4.1 .	395=1.8
Noord Brabant . .	41.155	9.173=22.3	1661=4.—	1072=2.6
Limburg	21.902	4.790=21 8	1013=4.7	497=2.2

TABLE II.

Municipality	Total	Redhaired	Percent.
the Hague. .	13.184	276	2.01
Enschede . .	3.667	77	2.1
Maastricht. .	3.812	86	2.2
Utrecht . . .	8.668	205	2.3
Haarlem . .	9.908	229	2.3
Hengelo. . .	2.876	68	2.3
Rotterdam. .	25.828	647	2.5
Amsterdam .	44.118	1164	2.6
Dordrecht . .	4.586	123	2.6
Zwolle . . .	3.618	101	2.7
Deventer . .	3.754	105	2.7
Leeuwarden .	3.562	102	2.8
Leiden	5.648	161	2.8
Gouda . . .	3.640	102	2.8
Groningen. .	5.039	142	2.8
Arnhem. . .	6.269	179	2.9

dam, the general figure of proportion, which has been found, reappears again.

Thus far I have left one province out of consideration, Zeeland. There is no denying that this province takes up a place somewhat separated from the others, since here the number of redhaired persons falls suddenly to 1.8%. This contrast with the other provinces is too great not to see here the influence of a definite cause. Yet this decrease in redhairiness in Zeeland, as will be proved higher up, cannot be attributed to a rise in the number of brunettes, which really occurs here, for N. Brabant, which is no less brunette than Zeeland, does not show this decrease. I will not enter into the cause of this decrease, I only wish to point out that already repeatedly both by Belgian and Dutch investigators attention has been drawn to the fact that from an anthropological point of view our Zeeland population takes up quite a peculiar place among the inhabitants of our country. It seems to me that this opinion is corroborated by the proportion found for the redhaired persons.

This much concerning the extension of redhaired persons in our country in general. The general conclusion to which we come, may be expressed thus, that with the exception of Zeeland this extension is a very regular one all through the country. This fact was really contrary to my expectation, as I myself, when beginning to work up my data, held the general opinion that there was a closer relationship between redhairiness and blondness. So I expected that, where in our country the blonde type varies so strongly, the influence of this would also come forth in the variation of redhairiness. Let us now, in order to prove the independence of the two phenomena, pay some more attention to Table I. For through this table we also get an insight into the decrease of the blonde and the increase of the brunette race, in a direction from North to South. As I said before, I distinguished on the schedules sent round four colours of hair and four of the eyes, making together 16 combinations. Of these combinations there are two which are really characteristical for the race, namely the combination blonde hair and blue eyes for the blonde race and the combination black hair and brown eyes for the brunette race. The other 14 combinations may be considered as mixed forms between the two races. Now, in order to keep the foundation of my reasoning as pure as possible, I have inserted in Table I only these two combinations to mutually compare them.

In the third column we find the number and percentage of blond-haired blue-eyed individuals in the different provinces. Now it appears that the number of pure blondes decreases very regularly from North

to South. The number is greatest in Friesland, viz. 43.8%, smallest in Limburg 21.8%, so reduced to half of the number for Friesland. The fourth column affords a survey of the increase of pure brunettes. Herein Drente shows the smallest number, 1.3 %, Limburg the greatest 4.6%. The figures in this column point to a distinct increase in a southern direction. From this table something else appears that is important for the characterisation of redhairiness. If namely the percentages of the "pure" types are added up, so the blondes and the brunettes, this gives for Friesland a total of 44.9%, for Limburg only 26.4%, while between these two numbers those of the other provinces are regularly grouped. So the number of mixed types is in the south of our country nearly 20% higher than in the north. As a general result we may state a decrease of the pure blondes, an increase of the pure brunettes and the mixed types in a southern direction.

And notwithstanding in Friesland twice as many pure blondes are found as in Limburg, a change in the number of redhaired individuals is not perceptible. Therefore I think I am entitled to deny the existence of any relation between the two phenomena on the ground of the figures found. But my table also induces me to reject the opinion which is sometimes given, that redhairiness should be a consequence of a crossing between a blonde and a brunette individual. If this were the case, an increase might be expected of the number of redhaired persons in a southern direction in connection with the increase of mixed types.

Have I therefore to deny relationship between the blonde and the redhaired type on the ground of the data mentioned, a still stronger proof for this is afforded by another fact, which I had expected as little as the others which have been explained. It is namely the extension of redhairiness among the Jewish school-population. The total number of Jewish children examined at Amsterdam, the Hague and Rotterdam amounted to 9155. Of these 228 were redhaired, i.e. 2.47 %, whilst for the not Jewish population a proportion of 2.45 % had been found. The agreement between the two figures is surprising and the importance of the fact for the question put by us, shows itself clearly, when I point out the fact that pure blondes i.e. blondhaired blue-eyed Jews occur only in a proportion of 8.2 % pure brunettes, i. e. black-haired brown-eyed in 18.1 %. From this it proceeds that in our country among the Jewish schoolpopulation with 8.2 % pure blondes, there occur as many redhaired persons as in Friesland with 43.2 % pure blondes. A stronger proof that there is no direct relation between redhairiness and blondness cannot be desired.

Thus far we examined redhairiness with regard to the increase or decrease of the number of blondes among our population, and we came to the conclusion that the two phenomena are independent of each other. We can now look upon the phenomena from another point of view. If it were true that redhairiness showed a preference for the blond race, the consequence of this must needs be that among the children who, as to pigmentation, belong to the blonde race, accordingly such as have blue or grey eyes, there are more redhaired individuals than among those with brown or brownishgreen eyes.

How far this is true is shown by Table III.

TABLE III.

Colour of eyes.	Total	Blondhaired	Brown	Black	Red
Blue . . .	186.033	83.34%	11.81%	2.38%	2.47%
Grey . . .	152.072	79.67	14.66	3.06	2.63
Brownish-green	58.531	60.68	28.64	8.—	2.55
Brown . .	82.338	45.05	38.61	14.28	2.03

The first column mentions the total number of children with one of the four different iris-colours, and in the four following columns we find consecutively the percentage of the combination of the iris-colour with one of the four haircolours. Phenomena make themselves manifest therein, which were to be expected beforehand. Of the blue-eyed individuals for example, 83 % have blonde hair, of the brown-eyed only 45 %; on the other hand the number of brown-haired persons with the last is more than three times as large as with the blue-eyed, and a relatively still stronger rise is found with the blackhaired. Generally speaking, it appears that with an increase of the pigmentation of the iris also the pigmentation of the hair increases. This holds good for blonde, brown and black hair. But in contradistinction to this there appears to be no relation between the degree of pigmentation of the iris and the hair with redhaired individuals. For of the blue-eyed 2.47 % are redhaired, of the grey-eyed 2.63 %, of the brownish-green-eyed 2.55 % and of the brown-eyed 2.03 %. It is true, this last figure is the lowest, but it seems to me that the difference is not so great that therein the proof may be seen that redhairiness shows less relationship to the brunette race. Moreover, this opinion could directly be refuted by the fact that I

find a somewhat lower percentage of redhaired individuals among the blue-eyed children than with the grey or brownish-greeneyed.

Red hair is therefore a quality altogether independent of the degree of pigmentation of the iris. No matter from what side we look upon the redhairiness with regard to the other phenomena of pigmentation of hair or eyes, there is — at least on the score of my researches — not a single proportion to be alleged on behalf of the opinion that redhairiness should by preference occur in the blonde race. So I cannot but reject as incorrect the opinion of those who, reducing redhairiness to a quantitative difference of pigment, see in it nothing but a nuance. And these results of our investigation naturally lead to considering red hair as a variety, in which the pigment is qualitatively different from that in blonde and black hair. Between these two last there is properly speaking no real difference; gradually, through numerous shades, flax-blonde hair passes into jet-black, by an increase of the quantity of pigment; also in red hair a great number of shades can be distinguished; in proportion to the quantity of pigment the colour varies between gold-blonde and fiery red.

How is the appearance and the regular extension of redhaired individuals among our population to be accounted for? It need hardly be said that, on the ground of the proportions found, I am not entitled to give any explanation. For this purpose anthropological researches of another nature would be necessary. Only for the sake of completeness I mention the opinion of TOPINARD, who explains redhairiness from a former mixing with an originally redhaired race, which in pre-historic times is said to have inhabited the plains of Russia, Siberia and Turkistan and of which one of the groups of the Finnish population (the Letts and the Esths) are said to be the purest descendants [1]).

[1]) L'histoire de cette race est à faire. Jusqu'à nouvel ordre j'admets qu'elle a occupé le sol de la Russie aux époques préhistoriques, antérieurement à l'invasion des Asiatiques, répondant à l'un des deux types finnois actuels, je n'ose dire de celui qui a apporté la langue du Kalevala. Elle est représentée dans la plupart des kourgans anciens de la Russie. Le type en est signalé dans les annales des Han antérieurement à l'ère chrétienne en Sibérie et dans le Turkestan Chinois. — Éléments d'Anthrop. générale. p. 334.

(November 28, 1907).

ERRATA.

Proceedings of the meeting of September 1907.

p. 229 l. 1 and p. 230 l. 7 from the bottom: for p. 1 read p. 215

Proceedings of the meeting of March 1907.

p. 788 l. 6 from the bottom: for $1.299 < \tau < 1.040$
read $1.299 > \tau > 1.040$

„ „ l. 5 „ „ „ for $1.040 < \tau < 1$
read $1.040 > \tau > 1$

„ „ l. 19 „ „ „ for "becomes" read "comes"

„ „ l. 18 „ „ „ for "united" read "unite"